The Asymmetric Synthesis of Amines
via Nickel-Catalyzed Enantioconvergent Substitution Reactions

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Supporting Information

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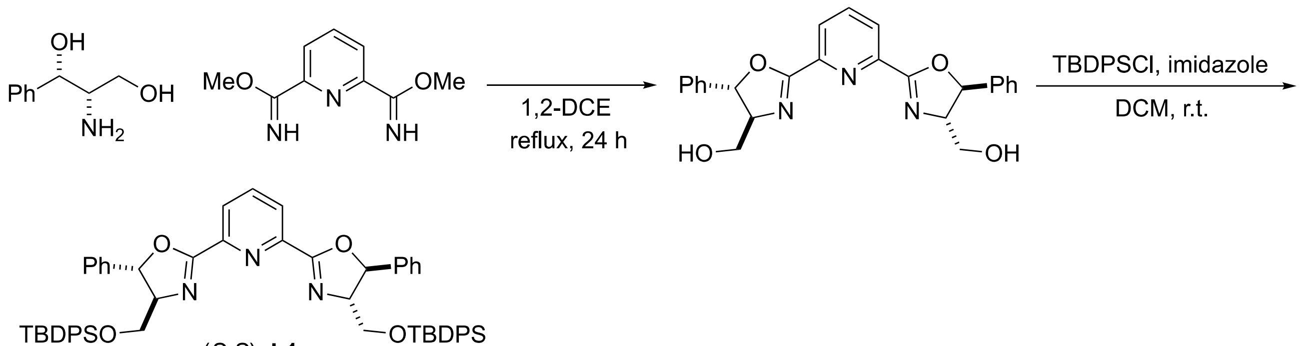
I. General Information

Unless otherwise noted, reagents received from commercial suppliers were used as received. All reactions were performed under an atmosphere of dry nitrogen. Anhydrous THF was purchased from Sigma-Aldrich and stored under nitrogen; other solvents were purified by passage through activated aluminum oxide in a solvent-purification system. Dimethyl pyridine-2,6-bis(carbimidate) was prepared from pyridine-2,6-dicarbonitrile.[1]

NMR spectra were collected on a Varian 300 MHz, a Bruker 400 MHz, or a Varian 500 MHz spectrometer at ambient temperature; chemical shifts (δ) are reported in ppm downfield from tertramethylsilane, using the solvent resonance as the internal standard. HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 5 μm). SFC analyses were carried out on an Agilent 1260 Infinity II system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 5 μm). FT-IR measurements were carried out on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory. HRMS were acquired by a Waters LCT Premier XE TOF MS in electrospray ionization (ESI+) mode. LC-MS were obtained on an Agilent 6140 UHPLC-MS system in electrospray ionization (ESI+) mode. Optical rotation data were obtained with a Jasco P-2000 polarimeter at 589 nm, using a 100 mm pathlength cell in the solvent and at the concentration indicated. GC analyses were carried out on an Agilent 6890N GC. Column chromatography was performed using silica gel (SiliaFlash® P60, particle size 40-63 μm, Silicycle) or acidic Al_2O_3 (Brockmann I, 50-200 μm, 60A, Acros Organics). X-ray crystallographic analyses were carried out by the Caltech X-Ray Crystallography Facility using a Bruker APEX-II CCD diffractometer. X-band EPR measurements were collected on a Bruker EMX spectrometer.

II. Preparation of Chiral Ligands

The yields have not been optimized.



(*S*,*S*)–**L1**

2,6-Bis((4*S*,5*S*)-4-(((*tert*-butyldiphenylsilyl)oxy)methyl)-5-phenyl-4,5-dihydrooxazol-2-yl)pyridine. An oven-dried 100 mL round-bottom flask was charged with a stir bar and fitted with a reflux condenser attached to a nitrogen line. Next, (1*S*,2*S*)-2-amino-1-phenylpropane-1,3-diol (5.05 g, 30.2 mmol, 2.0 equiv) and dimethyl pyridine-2,6-bis(carbimidate) (2.92 g, 15.1 mmol, 1.0 equiv) were added, and then the flask was sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and back-filling the flask (three cycles), followed by the addition of 1,2-dichloroethane (25 mL). The resulting solution was heated at reflux for 24 h. Then, the reaction mixture was cooled overnight at 5 °C, during which time ((4*S*,4'*S*,5*S*,5'*S*)-pyridine-2,6-diylbis(5-phenyl-4,5-dihydrooxazole-2,4-diyl))dimethanol precipitated as a brown solid, which was filtered, dried (4.67 g, 72% yield), and directly used in the following reaction.

A solution of ((4*S*,4'*S*,5*S*,5'*S*)-pyridine-2,6-diylbis(5-phenyl-4,5-dihydrooxazole-2,4-diyl))dimethanol (4.67 g, 10.9 mmol, 1.0 equiv), imidazole (4.45 g, 65.3 mmol, 6.0 equiv), and DCM (50 mL) was cooled to ~0 °C in an ice/water bath, and TBDPSCl (6.3 mL, 24 mmol, 2.2 equiv) was added via syringe over 5 min. The resulting mixture was stirred at room temperature for 4 h. Then, the reaction was quenched with water (50 mL), and the mixture was extracted with DCM (50 mL x 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (1:4 EtOAc/hexanes) to afford the product as a white solid (8.3 g, 9.2 mmol, 84% yield, >99% ee).

SFC analysis: The ee was determined via SFC on a CHIRALPAK IF-3 column (30% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for (*S*,*S*)-**L1**: 6.7 min, (*R*,*R*)-**L1**: 8.5 min.

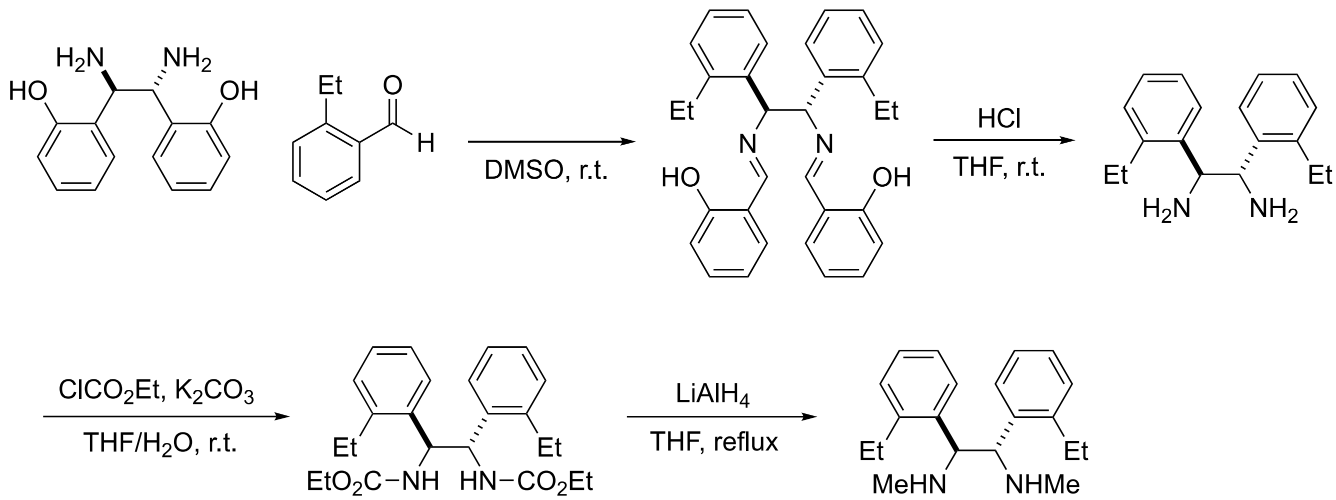
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.9 Hz, 2H), 7.89 (t, *J* = 7.9 Hz, 1H), 7.73 – 7.57 (m, 8H), 7.47 – 7.26 (m, 22H), 5.74 (d, *J* = 6.7 Hz, 2H), 4.50 – 4.37 (m, 2H), 4.13 – 4.04 (m, 2H), 3.93 – 3.76 (m, 2H), 1.05 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 147.2, 140.8, 137.4, 135.8, 135.7, 133.4, 133.3, 129.90, 129.87, 128.8, 128.3, 127.88, 127.87, 126.2, 126.1, 85.0, 76.8, 65.9, 27.0, 19.4.

FT-IR (film): 3419, 2932, 2740, 2355, 1962, 1644, 1574, 1462, 1428, 1360, 1256, 1218, 1112, 965, 825, 748 cm^{-1}.

HRMS (ESI+) m/z $[M+Na]^+$ calcd for $C_{57}H_{59}N_3NaO_4Si_2$: 928.3936, found: 928.3945.

$[\alpha]^{22}_D$ = +16.7 (*c* 1.0, $CHCl_3$), from (*S*,*S*)-**L1**.



(*S*,*S*)–**L2**

(1*S*,2*S*)-1,2-Bis(2-ethylphenyl)-*N¹*,*N²*-dimethylethane-1,2-diamine.[2] An oven-dried 250 mL round-bottom flask was charged with a stir bar and (*1R*,*2R*)-1,2-bis(2- hydroxyphenyl)-1,2-diaminoethane (10.0 g, 40.9 mmol, 1.0 equiv), and then it was sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and back-filling the flask (three cycles), followed by the addition of anhydrous DMSO (200 mL) and 2-ethylbenzaldehyde (13.7 g, 102 mmol, 2.5 equiv) via syringe. After the yellow mixture was stirred overnight at room temperature, the reaction was quenched by the addition of water (200 mL) and extracted with Et_2O (100 mL x 3). The combined organic layers were washed with water (100 mL) and brine (100 mL), and then they were dried over anhydrous Na_2SO_4 and filtered. The mixture was then concentrated under reduced pressure. 2,2'-((1*E*,1'*E*)-(((1*S*,2*S*)-1,2-Bis(2-ethylphenyl)ethane-1,2-diyl)bis(azanylylidene))bis-(methanylylidene))diphenol, obtained as a yellow oil as a mixture with unreacted 2-ethylbenzaldehyde, was used in the next step without further purification.

An oven-dried 1000 mL round-bottom flask was charged with a stir bar, and then it was sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and back-filling the flask (three cycles), followed by the addition of a solution of crude 2,2'-((1*E*,1'*E*)-(((1*S*,2*S*)-1,2-bis(2-ethylphenyl)ethane-1,2-diyl)bis(azanylylidene))bis-(methanylylidene))diphenol (~20 g, ~41 mmol) in THF (630 mL). A solution of HCl (12 M; 31 mL) was added to the reaction by addition funnel over 10 min while stirring at room temperature. The reaction was allowed to stir overnight, after which Et_2O (200 mL) was added. The diamine was extracted with a solution of HCl (1 M; 100 mL x 4). The combined aqueous phase was washed with Et_2O (100 mL) and was then basified with a solution of aqueous NaOH (2 M). The resulting yellow suspension was extracted with Et_2O (100 mL x 3).

The combined organic layers were washed with water (100 mL) and brine (100 mL), and then they were dried over anhydrous Na_2SO_4 and filtered. The mixture was concentrated under reduced pressure to give (1*S*,2*S*)-1,2-bis(2-ethylphenyl)ethane-1,2-diamine (9.2 g, 34 mmol, 82% yield over 2 steps) as an orange oil.

A 500 mL two-neck round-bottom flask was charged with a stir bar, a 250 mL addition funnel, and potassium carbonate (28.4 g, 206 mmol, 6.0 equiv), and then it was sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and back-filling the flask (three cycles). A solution of (1*S*,2*S*)-1,2-bis(2-ethylphenyl)ethane-1,2-diamine (9.2 g, 34 mmol, 1.0 equiv) in THF (275 mL) and distilled water (42 mL) were added sequentially via the addition funnel. After the resulting suspension was stirred for 10 min at room temperature, ethyl chloroformate (32.6 mL, 343 mmol, 10.0 equiv) was added dropwise into the flask via syringe over 10 min. The reaction was allowed to stir at room temperature for 4 days, after which it was diluted with distilled water (200 mL) and extracted with ethyl acetate (100 mL x 3). The combined organic layers were washed with water (150 mL) and brine (150 mL), and then they were dried over anhydrous Na_2SO_4 and filtered. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (3:7 EtOAc/hexanes) to afford diethyl ((1*S*,2*S*)-1,2-bis(2-ethylphenyl)ethane-1,2-diyl)dicarbamate as a white solid (3.7 g, 8.9 mmol, 26% yield).

An oven-dried 250 mL two-neck round-bottom flask was charged with a stir bar, fitted with a reflux condenser attached to a nitrogen manifold, and then sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and back-filling the flask (three cycles). Lithium aluminum hydride (1.6 g, 43 mmol, 5.0 equiv) was added through the open neck under a positive pressure of nitrogen. The open neck was capped with a rubber septum, and the flask was cooled to 0 °C using an ice/water bath. THF (40 mL) was added via syringe, and the gray suspension was stirred at 0 °C for 5 min. Next, a solution of diethyl ((1*S*,2*S*)-1,2-bis(2-ethylphenyl)ethane-1,2-diyl)dicarbamate (3.5 g, 8.6 mmol, 1.0 equiv) in THF (40 mL) was added dropwise via syringe through the rubber septum over 10 min. The ice/water bath was replaced with an oil bath, and the reaction mixture was heated at reflux for 18 h. The mixture was cooled to 0 °C using an ice/water bath, and water (4 mL) was added dropwise via syringe over 10 min. Next, a solution of aqueous NaOH (3.0 M; 4 mL) was added dropwise over 1 min. The resulting mixture was heated at reflux for 1 h, during which the color of the precipitate changed from gray to white. The warm solution was filtered through a Büchner funnel that contained a bed of celite, and the precipitate was washed with Et_2O (100 mL). The filtrate was concentrated under reduced pressure to yield the crude product as a light-yellow solid. The crude product was dissolved in EtOH (30 mL) and *D*-tartaric acid (1.29 g, 8.6 mmol, 1.0 equiv) was added. The heterogeneous mixture was stirred at reflux for 30 min, after which it was allowed to slowly cool back to room temperature. The mixture was then cooled to 0 °C, and after 4 h the precipitate was collected by filtration and washed with EtOH (5 mL x 2). The precipitate was added to a mixture of 10% NaOH in water (10 mL) and Et_2O (10 mL). After stirring overnight, the layers were separated, and the aqueous layers were extracted with Et_2O (10 mL x 2). The combined organic layers were washed with water (20 mL) and brine (20 mL), and then they were dried over anhydrous Na_2SO_4 and filtered. The mixture was concentrated under reduced pressure to yield the desired ligand as a white solid (1.59 g, 5.4 mmol, 62% yield, >99% ee).

SFC analysis: The ee was determined via SFC on a CHIRALPAK ID column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for (*S*,*S*)-**L2**: 3.2 min, (*R*,*R*)-**L2**: 4.2 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.15 (td, *J* = 7.5, 1.5 Hz, 2H), 7.07 (td, *J* = 7.4, 1.5 Hz, 2H), 6.91 (dd, *J* = 7.6, 1.5 Hz, 2H), 3.91 (s, 2H), 2.46 – 2.33 (m, 2H), 2.23 (s, 6H), 2.12 – 2.00 (m, 4H), 0.95 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 138.8, 128.2, 127.0, 126.8, 125.8, 65.3, 34.8, 24.7, 15.5.

FT-IR (film): 3230, 2967, 2786, 1489, 1106, 874, 764, 741 cm^{-1}.

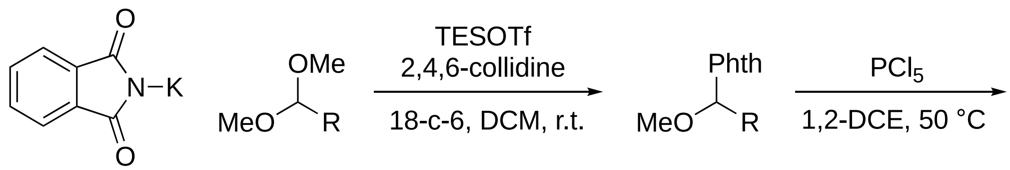
LC-MS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{29}N_2$: 297.2, found: 297.2.

$[\alpha]^{23}_D$ = +13.2 (*c* 1.0, $CHCl_3$), from (*S*,*S*)-**L2**.

III. Preparation of Electrophiles

The yields have not been optimized.

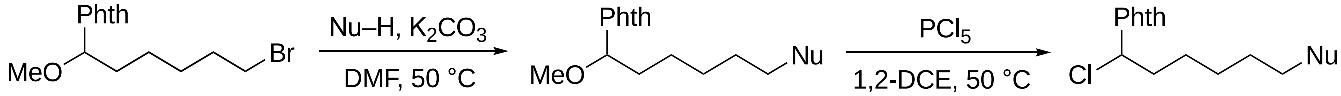
General Procedure 1 (GP-1).



Preparation of *N,O*-acetals. An oven-dried 250 mL round-bottom flask was charged with a stir bar and the acetal (1.0 equiv; either purchased or prepared from the corresponding aldehyde[3]), and then it was sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and back-filling the flask (three cycles), and then DCM (volume to generate a 1.0 M solution of the potassium phthalimide) and 2,4,6-collidine (3.0 equiv) were added. The resulting solution was cooled to ~0 °C using an ice/water bath, and then TESOTf (2.0 equiv) was added via syringe over 10 min. The reaction mixture was stirred at ~0 °C for 30 min. After verifying the consumption of the acetal via TLC, potassium phthalimide (3.0 equiv) and 18-crown-6 (3.0 equiv) were added in one portion to the reaction mixture under a positive flow of nitrogen, and the solution was stirred at room temperature for 2 h. Then, the reaction was quenched with water, and the mixture was extracted with DCM (three times). The combined organic layers were washed with a solution of HCl (2 M), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the *N,O*-acetal.

Chlorination of *N,O*-acetals. PCl_5 (1.5 equiv) was added to a solution of the *N,O*-acetal (1.0 M in 1,2-DCE; 1.0 equiv) at room temperature. The reaction mixture was stirred at 50 °C overnight, and then the reaction was quenched with water. The organic layer was washed with saturated aqueous $NaHCO_3$ (three times), and then it was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product was purified either by recrystallization ($CHCl_3$/hexanes) or by column chromatography on acidic Al_2O_3. The alkyl chlorides used in this study are stable after purification and can be stored at room temperature for at least six months without decomposition.

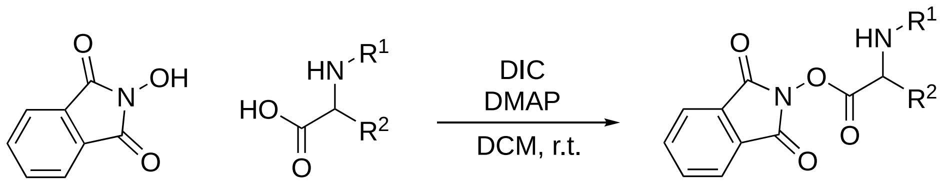
General Procedure 2 (GP-2).



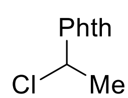
Preparation of *N,O*-acetals. K_2CO_3 (1.3 equiv) and the nucleophile (1.3 equiv) were added to solution of 2-(6-bromo-1-methoxyhexyl)isoindoline-1,3-dione (0.50 M in DMF; 1.0 equiv; synthesized according to the first step of **GP-1**). The reaction mixture was stirred at 50 °C overnight. Then, the reaction was quenched with water, and the mixture was extracted with DCM (three times). The combined organic layers were washed with water and brine, and then they were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the *N*,*O*-acetal.

Chlorination of *N*,*O*-acetals. See **GP-1**.

General Procedure 3 (GP-3).



Preparation of NHP esters. An oven-dried 250 mL round-bottom flask was charged with a stir bar, *N*-hydroxyphthalimide (1.0 equiv), and DMAP (1.0 equiv), and then it was sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and back-filling the flask (three cycles), followed by the addition of anhydrous DCM (volume to generate a 0.2 M solution of the amino acid) via syringe. The mixture was stirred for 5 min, after which the amino acid (1.0 equiv) was added under a positive flow of nitrogen. After the mixture had stirred for an additional 5 min, DIC (1.0 equiv) was added dropwise via syringe over 5 min. The reaction was allowed to stir until the acid was fully consumed (typically 1 h, although the reaction can be left to stir overnight with no significant loss in yield). The mixture was filtered through a pad of celite and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and filtered, and the solution was then concentrated under reduced pressure. Methanol (~5.0 mL/mmol of the amino acid) was added, and the mixture was stirred for 5 min. The mixture was cooled to –25 °C over 4 h, during which a solid precipitated. The solid was filtered and washed with cold methanol, affording the desired NHP ester. The NHP esters used in this study can be stored at room temperature for over one year without decomposition.



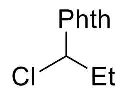
2-(1-Chloroethyl)isoindoline-1,3-dione. The title compound was synthesized according to **GP-1** from 1,1-dimethoxyethane (1.80 g, 20.0 mmol). The product was purified by recrystallization. 2.91 g (14.3 mmol, 72% yield over 2 steps). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.84 (m, 2H), 7.84 – 7.71 (m, 2H), 6.29 (q, *J* = 6.8 Hz, 1H), 2.16 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 134.8, 131.7, 124.0, 60.3, 23.5.

FT-IR (film): 3444, 2916, 2354, 1715, 1360, 1033, 876, 721 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M+Na]$^+$ calcd for $C_{10}H_8ClNNaO_2$: 232.0, found: 232.2.



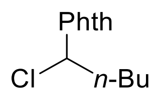
2-(1-Chloropropyl)isoindoline-1,3-dione. The title compound was synthesized according to **GP-1** from 1,1-dimethoxypropane (3.12 g, 30.0 mmol). The product was purified by recrystallization. 4.48 g (20.1 mmol, 67% yield over 2 steps). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.85 (m, 2H), 7.82 – 7.73 (m, 2H), 5.99 (t, *J* = 7.6 Hz, 1H), 2.66 – 2.46 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 134.8, 131.7, 124.0, 65.7, 29.7, 11.3.

FT-IR (film): 2978, 2370, 1724, 1458, 1373, 1293, 1064, 1032, 870, 720 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+NH_4]^+$ calcd for $C_{11}H_{14}ClN_2O_2$: 241.1, found: 241.1.



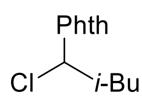
2-(1-Chloropentyl)isoindoline-1,3-dione. The title compound was synthesized according to **GP-1** from 1,1-dimethoxypentane (2.35 g, 17.8 mmol). The product was purified by recrystallization. 2.60 g (10.4 mmol, 58% yield over 2 steps). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.84 (m, 2H), 7.84 – 7.70 (m, 2H), 6.07 (t, *J* = 7.7 Hz, 1H), 2.66 – 2.41 (m, 2H), 1.54 – 1.21 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 134.8, 131.7, 124.0, 64.3, 35.9, 28.8, 21.9, 14.0.

FT-IR (film): 3495, 2960, 2369, 1732, 1469, 1366, 1073, 959, 879, 726 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M-Cl]^+$ calcd for $C_{13}H_{14}NO_2$: 216.1, found: 216.1.



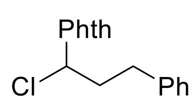
2-(1-Chloro-3-methylbutyl)isoindoline-1,3-dione. The title compound was synthesized according to **GP-1** from 1,1-dimethoxy-3-methylbutane (2.64 g, 20.0 mmol). The product was purified by column chromatography on acidic Al_2O_3 (1:3 EtOAc/hexanes). 2.52 g (10.0 mmol, 50% yield over 2 steps). Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.84 (m, 2H), 7.83 – 7.70 (m, 2H), 6.19 (dd, *J* = 8.3, 7.3 Hz, 1H), 2.59 – 2.45 (m, 1H), 2.41 – 2.27 (m, 1H), 1.78 – 1.61 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 134.8, 131.7, 124.0, 63.0, 44.5, 25.9, 22.2, 22.0.

FT-IR (film): 3487, 2915, 2351, 1723, 1360, 1049, 952, 882, 741 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M-Cl]^+$ calcd for $C_{13}H_{14}NO_2$: 216.1, found: 216.1.



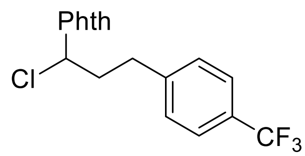
2-(1-Chloro-3-phenylpropyl)isoindoline-1,3-dione. The title compound was synthesized according to **GP-1** from (3,3-dimethoxypropyl)benzene (3.60 g, 20.0 mmol). The product was purified by recrystallization. 4.10 g (13.7 mmol, 69% yield over 2 steps). White solid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.83 (m, 2H), 7.81 – 7.72 (m, 2H), 7.29 – 7.20 (m, 2H), 7.20 – 7.09 (m, 3H), 6.07 (t, *J* = 7.4 Hz, 1H), 3.00 – 2.77 (m, 3H), 2.77 – 2.64 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 139.6, 134.8, 131.7, 128.7, 128.6, 126.5, 124.0, 63.7, 37.4, 33.0.

FT-IR (film): 3488, 3027, 2352, 1721, 1360, 1222, 1081, 966, 876, 736 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M-Cl]$^+$ calcd for $C_{17}H_{14}NO_2$: 264.1, found: 264.1.



2-(1-Chloro-3-(4-(trifluoromethyl)phenyl)propyl)isoindoline-1,3-dione. The title compound was synthesized according to **GP-1** from 1-(3,3-dimethoxypropyl)-4-(trifluoromethyl)benzene (4.96 g, 20.0 mmol). The product was purified by recrystallization. 5.41 g (14.7 mmol, 74% yield over 2 steps). White solid.

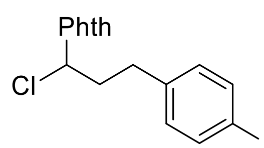
^1H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.80 – 7.71 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 6.06 (t, *J* = 7.3 Hz, 1H), 3.03 – 2.81 (m, 3H), 2.82 – 2.69 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 143.6, 134.9, 131.4, 128.9, 128.8 (q, *J* = 26.3 Hz), 125.5 (q, *J* = 3.0 Hz), 124.2 (q, *J* = 218 Hz), 123.9, 63.4, 36.9, 32.9.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.4.

FT-IR (film): 3495, 2938, 2357, 1731, 1360, 1068, 1019, 719 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M-Cl]$^+$ calcd for $C_{18}H_{13}F_3NO_2$: 332.1, found: 332.1.



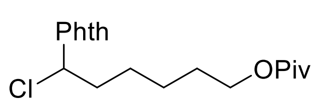
2-(1-Chloro-3-(4-iodophenyl)propyl)isoindoline-1,3-dione. The title compound was synthesized according to **GP-1** from 1-(3,3-dimethoxypropyl)-4-iodobenzene (4.08 g, 13.3 mmol). The product was purified by recrystallization. 3.4 g (8.0 mmol, 60% yield over 2 steps). White solid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.82 (m, 2H), 7.82 – 7.73 (m, 2H), 7.59 – 7.49 (m, 2H), 6.94 – 6.85 (m, 2H), 6.04 (t, *J* = 7.4 Hz, 1H), 2.97 – 2.71 (m, 3H), 2.69 – 2.57 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 139.2, 137.7, 134.9, 131.6, 130.6, 124.0, 91.7, 63.5, 37.0, 32.6.

FT-IR (film): 3484, 2937, 2351, 1722, 1366, 1087, 722 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M-Cl]$^+$ calcd for $C_{17}H_{13}INO_2$: 390.0, found: 390.0.



6-Chloro-6-(1,3-dioxoisoindolin-2-yl)hexyl pivalate. The title compound was synthesized according to **GP-1** from methyl 6,6-dimethoxyhexyl pivalate (4.10 g, 16.7 mmol).

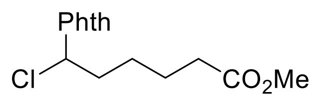
The product was purified by column chromatography on acidic Al_2O_3 (1:4 EtOAc/hexanes). 2.1 g (5.8 mmol, 34% yield over 2 steps). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.85 (m, 2H), 7.81 – 7.73 (m, 2H), 6.06 (t, J = 7.7 Hz, 1H), 4.02 (t, J = 6.5 Hz, 2H), 2.64 – 2.46 (m, 2H), 1.66 – 1.57 (m, 2H), 1.57 – 1.30 (m, 4H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 166.5, 134.8, 131.7, 124.0, 64.2, 64.1, 38.8, 36.1, 28.5, 27.3, 26.4, 25.2.

FT-IR (film): 3496, 2920, 2354, 1726, 1461, 1362, 1148, 1049, 883, 738 cm^{-1}.

LC-MS (ESI-MS) m/z [M-Cl]$^+$ calcd for $C_{19}H_{24}NO_4$: 330.2, found: 330.2.



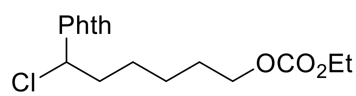
Methyl 6-chloro-6-(1,3-dioxoisoindolin-2-yl)hexanoate. The title compound was synthesized according to **GP-1** from methyl 6,6-dimethoxyhexanoate (3.60 g, 18.9 mmol). The product was purified by column chromatography on acidic Al_2O_3 (1:4 EtOAc/hexanes). 1.4 g (4.5 mmol, 24% yield over 2 steps). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.85 (m, 2H), 7.83 – 7.69 (m, 2H), 6.06 (t, J = 7.6 Hz, 1H), 3.64 (s, 3H), 2.55 (q, J = 7.7 Hz, 2H), 2.31 (t, J = 7.4 Hz, 2H), 1.74 – 1.61 (m, 2H), 1.59 – 1.45 (m, 1H), 1.44 – 1.31 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 166.4, 134.8, 131.7, 124.0, 64.0, 51.7, 35.8, 33.8, 26.2, 24.0.

FT-IR (film): 3494, 2950, 2356, 1731, 1360, 1214, 1052, 879, 728 cm^{-1}.

LC-MS (ESI-MS) m/z [M-Cl]$^+$ calcd for $C_{15}H_{16}NO_4$: 274.1, found: 274.1.



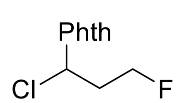
6-Chloro-6-(1,3-dioxoisoindolin-2-yl)hexyl ethyl carbonate. The title compound was synthesized according to **GP-1** from 6,6-dimethoxyhexyl ethyl carbonate (4.68 g, 20.0 mmol). The product was purified by column chromatography on acidic Al_2O_3 (1:3 EtOAc/hexanes). 2.63 g (7.45 mmol, 37% yield over 2 steps). Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.83 (m, 2H), 7.83 – 7.70 (m, 2H), 6.05 (t, J = 7.6 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.10 (t, J = 6.5 Hz, 2H), 2.64 – 2.46 (m, 2H), 1.73 – 1.60 (m, 2H), 1.59 – 1.33 (m, 4H), 1.29 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 155.3, 134.8, 131.7, 124.0, 67.6, 64.1, 64.0, 36.0, 28.5, 26.3, 25.0, 14.4.

FT-IR (film): 3499, 2912, 2354, 1728, 1358, 1011, 879, 729 cm^{-1}.

LC-MS (ESI-MS) m/z [M-Cl]$^+$ calcd for $C_{17}H_{20}NO_5$: 318.1, found: 318.1.



2-(1-Chloro-3-fluoropropyl)isoindoline-1,3-dione. The title compound was synthesized according to **GP-1** from 3-fluoro-1,1-dimethoxypropane (1.22 g, 10.0 mmol). The product was purified by recrystallization. 0.54 g (2.2 mmol, 22% yield over 2 steps). White solid.

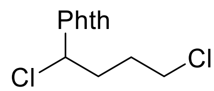
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.86 (m, 2H), 7.86 – 7.72 (m, 2H), 6.32 (dd, *J* = 8.5, 6.2 Hz, 1H), 4.80 – 4.44 (m, 2H), 3.11 – 2.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 134.9, 131.7, 124.1, 80.3 (d, *J* = 168 Hz), 60.8 (d, *J* = 5.1 Hz), 37.0 (d, *J* = 19.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ –220.8.

FT-IR (film): 3493, 2972, 2353, 1731, 1470, 1360, 1058, 901, 721 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M-Cl]^+$ calcd for $C_{11}H_9FNO_2$: 206.1, found: 206.1.



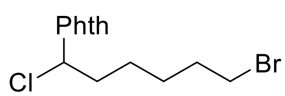
2-(1,4-Dichlorobutyl)isoindoline-1,3-dione. The title compound was synthesized according to **GP-1** from 4-chloro-1,1-dimethoxybutane (3.04 g, 20.0 mmol). The product was purified by recrystallization. 2.66 g (9.82 mmol, 49% yield over 2 steps). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.84 (m, 2H), 7.84 – 7.71 (m, 2H), 6.09 (t, *J* = 7.6 Hz, 1H), 3.69 – 3.48 (m, 2H), 2.84 – 2.59 (m, 2H), 2.09 – 1.93 (m, 1H), 1.93 – 1.77 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 134.9, 131.6, 124.1, 63.5, 43.7, 33.5, 29.7.

FT-IR (film): 3486, 2964, 2358, 1731, 1372, 1106, 883, 720 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M-Cl]^+$ calcd for $C_{12}H_{11}ClNO_2$: 236.0, found: 236.1.



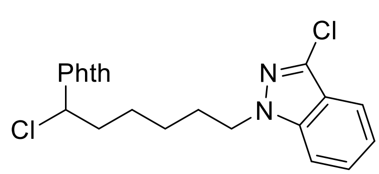
2-(6-Bromo-1-chlorohexyl)isoindoline-1,3-dione. The title compound was synthesized according to **GP-1** from 6-bromo-1,1-dimethoxyhexane (4.48 g, 20.0 mmol). The product was purified by recrystallization. 2.5 g (7.3 mmol, 36% yield over 2 steps). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 2H), 7.86 – 7.70 (m, 2H), 6.07 (t, *J* = 7.7 Hz, 1H), 3.38 (t, *J* = 6.7 Hz, 2H), 2.66 – 2.46 (m, 2H), 1.95 – 1.77 (m, 2H), 1.57 – 1.44 (m, 3H), 1.44 – 1.30 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 134.8, 131.7, 124.0, 64.1, 35.9, 33.5, 32.5, 27.3, 25.9.

FT-IR (film): 3490, 2936, 2354, 1728, 1358, 1038, 878, 720 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M-Cl]^+$ calcd for $C_{14}H_{15}BrNO_2$: 308.0, found: 308.0.



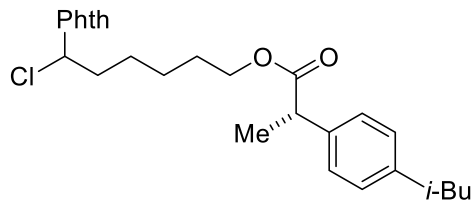
2-(1-Chloro-6-(3-chloro-1*H*-indazol-1-yl)hexyl)isoindoline-1,3-dione. The title compound was synthesized according to **GP-2** from 2-(6-bromo-1-methoxyhexyl)isoindoline-1,3-dione (2.37 g, 6.99 mmol) and 3-chloro-1*H*-indazole (1.39 g, 9.14 mmol). The product was purified by recrystallization. 1.7 g (4.1 mmol, 59% yield over 2 steps). Yellow solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 – 7.83 (m, 2H), 7.82 – 7.72 (m, 2H), 7.69 – 7.60 (m, 1H), 7.45 – 7.31 (m, 2H), 7.22 – 7.13 (m, 1H), 6.03 (t, *J* = 7.7 Hz, 1H), 4.30 (t, *J* = 7.0 Hz, 2H), 2.64 – 2.40 (m, 2H), 2.04 – 1.83 (m, 2H), 1.55 – 1.43 (m, 1H), 1.44 – 1.28 (m, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 166.3, 140.8, 134.7, 132.6, 131.5, 127.4, 123.9, 121.1, 121.0, 119.9, 109.2, 63.9, 48.9, 35.8, 29.5, 26.2, 25.9.

FT-IR (film): 3492, 2936, 2354, 1731, 1469, 1360, 1046, 879, 746 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M-Cl]$^+$ calcd for $C_{21}H_{19}ClN_3O_2$: 380.1, found: 380.1.



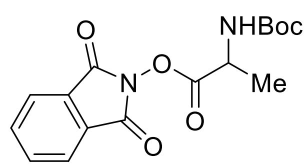
6-Chloro-6-(1,3-dioxoisoindolin-2-yl)hexyl (2*S*)-2-(4-isobutylphenyl)propanoate. The title compound was synthesized according to **GP-2** from 2-(6-bromo-1-methoxyhexyl)isoindoline-1,3-dione (2.37 g, 6.99 mmol) and (*S*)-2-(4-isobutylphenyl)propanoic acid (1.87 g, 9.08 mmol). The product was purified by column chromatography on acidic Al_2O_3 (1:4 EtOAc/hexanes). 1.4 g (3.0 mmol, 43% yield over 2 steps). Colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 – 7.85 (m, 2H), 7.82 – 7.73 (m, 2H), 7.22 – 7.15 (m, 2H), 7.12 – 7.05 (m, 2H), 6.03 (t, *J* = 7.7 Hz, 1H), 4.03 (t, *J* = 5.9 Hz, 2H), 3.67 (q, *J* = 7.2 Hz, 1H), 2.56 – 2.39 (m, 4H), 1.92 – 1.74 (m, 1H), 1.64 – 1.51 (m, 2H), 1.51 – 1.37 (m, 4H), 1.38 – 1.23 (m, 3H), 0.87 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 174.9, 166.5, 140.6, 138.0, 134.8, 131.7, 129.4, 127.3, 124.0, 64.42, 64.40, 64.1, 45.3, 45.1, 36.0, 30.3, 28.4, 26.3, 25.0, 22.5, 18.5.

FT-IR (film): 3494, 2915, 2355, 1728, 1359, 1029, 727, 681 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M-Cl]$^+$ calcd for $C_{27}H_{32}NO_4$: 434.2, found: 434.2.



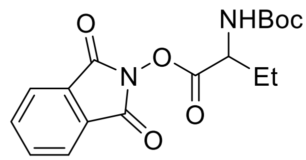
1,3-Dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)alaninate. The title compound was synthesized according to **GP-3** from (*tert*-butoxycarbonyl)alanine (1.91 g, 10.1 mmol). 1.28 g (3.83 mmol, 38% yield). White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 – 7.85 (m, 2H), 7.85 – 7.75 (m, 2H), 5.23 – 4.98 (m, 1H), 4.86 – 4.44 (m, 1H), 1.63 (d, *J* = 7.2 Hz, 3H), 1.56 – 1.40 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 170.1, 161.6, 154.9, 134.8, 128.9, 124.0, 80.7, 47.9, 28.4, 19.1.

FT-IR (film): 3356, 2978, 1749, 1368, 1162, 1050, 878, 753, 698 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M+Na]$^+$ calcd for $C_{16}H_{18}N_2NaO_6$: 357.1, found: 357.1.



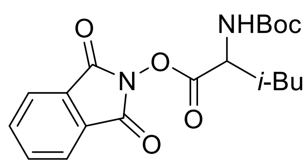
1,3-Dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)butanoate. The title compound was synthesized according to **GP-3** from 2-((*tert*-butoxycarbonyl)amino)butanoic acid (5.00 g, 24.6 mmol). 1.76 g (5.06 mmol, 21% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (m, 2H), 7.85 – 7.75 (m, 2H), 5.05 (d, J = 8.7 Hz, 1H), 4.75 – 4.68 (m, 1H), 2.00 (m, 2H), 1.49 (s, 9H), 1.24 – 1.07 (t, J = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 161.6, 155.0, 135.0, 129.0, 124.1, 80.6, 53.2, 28.4, 26.5, 9.4.

FT-IR (film): 3370, 2976, 1789, 1747, 1367, 1167, 1063, 877, 682 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{17}H_{20}N_2NaO_6$: 371.1, found: 371.1.



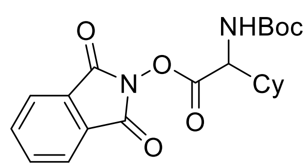
1,3-Dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)leucinate. The title compound was synthesized according to **GP-3** from (*tert*-butoxycarbonyl)leucine (5.00 g, 21.6 mmol). 5.63 g (15.0 mmol, 69% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.84 – 7.74 (m, 2H), 4.93 (d, J = 8.9 Hz, 1H), 4.83 – 4.66 (m, 1H), 1.95 – 1.81 (m, 2H), 1.77 – 1.65 (m, 1H), 1.50 (s, 9H), 1.05 – 0.99 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 161.6, 155.0, 134.9, 128.9, 124.1, 80.6, 50.7, 41.9, 28.4, 24.8, 22.9, 21.9.

FT-IR (film): 3386, 2962, 1747, 1367, 1166, 1081, 968, 698 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{24}N_2NaO_6$: 399.2, found 399.1.



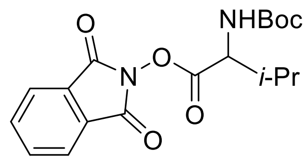
1,3-Dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetate. The title compound was synthesized according to **GP-3** from 2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetic acid (6.00 g, 23.3 mmol). 6.78 g (16.8 mmol, 72% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.83 (m, 2H), 7.83 – 7.74 (m, 2H), 5.05 (d, *J* = 9.4 Hz, 1H), 4.68 – 4.60 (m, 1H), 2.05 – 1.92 (m, 1H), 1.90 – 1.78 (m, 4H), 1.74 – 1.65 (m, 1H), 1.47 (s, 9H), 1.40 – 1.11 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 161.7, 155.2, 134.9, 129.0, 124.1, 80.5, 56.9, 41.4, 29.2, 28.4, 26.0.

FT-IR (film): 3275, 2932, 1747, 1366, 1162, 972, 877, 754, 697 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{21}H_{26}N_2NaO_6$: 425.2, found: 425.1.



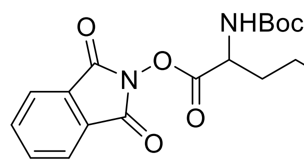
1,3-Dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)valinate. The title compound was synthesized according to **GP-3** from (*tert*-butoxycarbonyl)valine (4.50 g, 20.7 mmol). 2.79 g (7.71 mmol, 37% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.84 – 7.74 (m, 2H), 5.05 (d, *J* = 9.4 Hz, 1H), 4.70 – 4.62 (m, 1H), 2.42 – 2.28 (m, 1H), 1.47 (s, 9H), 1.17 – 1.05 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 161.7, 155.3, 134.9, 129.0, 124.1, 80.5, 57.2, 31.9, 28.4, 18.9, 17.5.

FT-IR (film): 3369, 2974, 1743, 1366, 1166, 1072, 970, 759, 697 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M+Na]$^+$ calcd for $C_{18}H_{22}N_2NaO_6$: 385.1, found: 385.1.



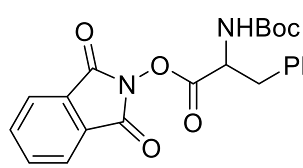
1,3-Dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate. The title compound was synthesized according to **GP-3** from 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoic acid (3.00 g, 10.7 mmol). 3.08 g (7.26 mmol, 68% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.85 – 7.76 (m, 2H), 7.36 – 7.18 (m, 5H), 5.07 (d, *J* = 8.7 Hz, 1H), 4.85 – 4.75 (m, 1H), 2.89 – 2.78 (m, 2H), 2.42 – 2.11 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 161.6, 154.9, 140.5, 135.0, 129.0, 128.73, 128.65, 126.4, 124.2, 80.7, 51.9, 34.9, 31.4, 28.4.

FT-IR (film): 3374, 2976, 1789, 1746, 1368, 1166, 759, 697 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M+Na]$^+$ calcd for $C_{23}H_{24}N_2NaO_6$: 447.2, found: 447.1.



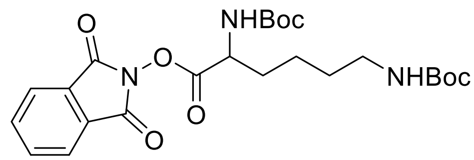
1,3-Dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)phenylalaninate. The title compound was synthesized according to **GP-3** from (*tert*-butoxycarbonyl)phenylalanine (4.50 g, 17.0 mmol). 3.59 g (8.76 mmol, 52% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.85 (m, 2H), 7.84 – 7.75 (m, 2H), 7.43 – 7.25 (m, 5H), 5.10 – 4.58 (m, 2H), 3.42 – 3.12 (m, 2H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 161.5, 154.7, 135.0, 129.8, 129.7, 128.9, 128.8, 127.4, 124.1, 80.6, 52.8, 38.3, 28.3.

FT-IR (film): 3349, 2977, 1747, 1710, 1514, 1366, 1172, 753, 698 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M+Na]$^+$ calcd for $C_{22}H_{22}N_2NaO_6$: 433.1, found: 433.1.



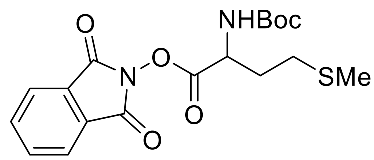
1,3-Dioxoisoindolin-2-yl *N*²,*N*⁶-bis(*tert*-butoxycarbonyl)lysinate. The title compound was synthesized according to **GP-3** from *N*²,*N*⁶-bis(*tert*-butoxycarbonyl)lysine (5.49 g, 15.9 mmol). 1.07 g (2.18 mmol, 14% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.82 – 7.78 (m, 2H), 5.22 – 4.86 (m, 1H), 4.68 – 4.44 (m, 2H), 3.22 – 3.12 (m, 2H), 2.05 – 1.87 (m, 2H), 1.57 – 1.41 (m, 22H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 161.7, 156.3, 155.1, 135.0, 129.0, 124.2, 80.7, 79.3, 52.0, 40.0, 32.4, 29.6, 28.6, 28.4, 22.1.

FT-IR (film): 3356, 2977, 1747, 1709, 1518, 1366, 1174, 759, 697 cm^{-1}.

LC-MS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{24}H_{33}N_3NaO_8$: 514.2, found: 514.2.



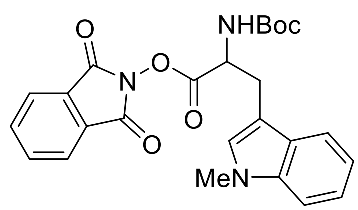
1,3-Dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)methioninate. The title compound was synthesized according to **GP-3** from (*tert*-butoxycarbonyl)methionine (5.35 g, 21.5 mmol). 4.87 g (12.4 mmol, 58% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.84 – 7.75 (m, 2H), 5.23 – 5.04 (m, 1H), 4.94 – 4.61 (m, 1H), 2.77 – 2.62 (m, 2H), 2.36 – 2.12 (m, 5H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 161.5, 154.9, 135.0, 128.9, 124.1, 80.7, 51.4, 32.4, 29.6, 28.3, 15.5.

FT-IR (film): 3370, 2978, 1747, 1367, 1186, 968, 758, 698 cm^{-1}.

LC-MS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{18}H_{22}N_2NaO_6S$: 417.1, found 417.1.



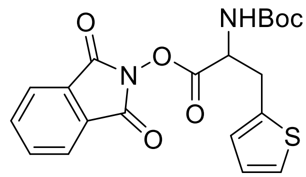
1,3-Dioxoisoindolin-2-yl *N*$^\alpha$-(*tert*-butoxycarbonyl)-1-methyltryptophanate. The title compound was synthesized according to **GP-3** from *N*$^\alpha$-(*tert*-butoxycarbonyl)-1-methyltryptophan (2.2 g, 6.9 mmol). 1.2 g (2.5 mmol, 37% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.84 – 7.77 (m, 2H), 7.67 – 7.58 (m, 1H), 7.35 – 7.27 (m, 2H), 7.27 – 7.09 (m, 2H), 5.20 – 4.59 (m, 2H), 3.80 (s, 3H), 3.62 – 3.29 (m, 2H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 161.7, 154.9, 137.0, 134.9, 129.0, 128.7, 124.2, 121.8, 119.4, 118.9, 109.4, 107.0, 80.4, 53.5, 32.9, 28.4, 28.1, 27.9.

FT-IR (film): 3380, 2978, 1731, 1486, 1371, 1166, 972, 754, 697 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{25}H_{25}N_3NaO_6$: 486.2, found: 486.2.



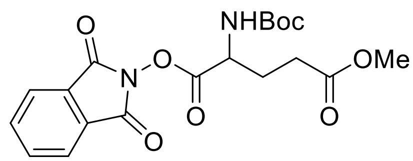
1,3-Dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-3-(thiophen-2-yl)propanoate. The title compound was synthesized according to **GP-3** from 2-((*tert*-butoxycarbonyl)amino)-3-(thiophen-2-yl)propanoic acid (4.00 g, 14.7 mmol). 3.28 g (7.88 mmol, 54% yield). Light-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.82 – 7.79 (m, 2H), 7.26 – 7.19 (m, 1H), 7.11 – 7.06 (m, 1H), 7.00 (dd, *J* = 5.2, 3.5 Hz, 1H), 5.15 – 4.69 (m, 2H), 3.62 – 3.51 (m, 2H), 1.47 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 161.5, 154.7, 136.1, 135.0, 134.0, 128.9, 127.8, 127.5, 125.3, 124.2, 123.2, 80.8, 52.9, 32.5, 28.4.

FT-IR (film): 3369, 2978, 1746, 1720, 1368, 1162, 970, 758, 697 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{20}H_{20}N_2NaO_6S$: 439.1, found: 439.1.



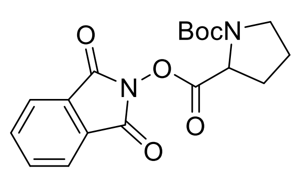
1-(1,3-Dioxoisoindolin-2-yl) 5-methyl (*tert*-butoxycarbonyl)glutamate. The title compound was synthesized according to **GP-3** from 2-((*tert*-butoxycarbonyl)amino)-5-methoxy-5-oxopentanoic acid (0.68 g, 2.6 mmol). 0.53 g (1.3 mmol, 51% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.86 – 7.76 (m, 2H), 5.28 – 5.04 (m, 1H), 4.89 – 4.49 (m, 1H), 3.72 (s, 3H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.40 – 2.24 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 169.1, 161.6, 155.0, 135.0, 128.9, 124.2, 80.8, 52.1, 51.6, 29.8, 28.4, 28.0.

FT-IR (film): 3368, 2978, 1789, 1746, 1368, 1164, 878, 697 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{22}N_2NaO_8$: 429.1, found: 429.1.



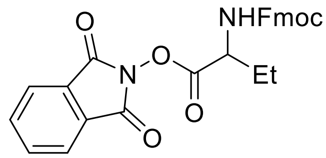
1-(*tert*-Butyl) 2-(1,3-dioxoisoindolin-2-yl) pyrrolidine-1,2-dicarboxylate. The title compound was synthesized according to **GP-3** from (*tert*-butoxycarbonyl)proline (3.00 g, 13.9 mmol). 1.41 g (3.92 mmol, 28% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.83 (m, 2H), 7.83 – 7.73 (m, 2H), 4.65 – 4.57 (m, 1H), 3.69 – 3.37 (m, 2H), 2.51 – 2.30 (m, 2H), 2.13 – 1.92 (m, 2H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 161.8, 153.5, 134.9, 128.9, 124.0, 81.2, 57.3, 46.3, 31.5, 28.2, 23.6.

FT-IR (film): 2977, 1745, 1394, 1163, 1069, 972, 757, 697 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{20}N_2NaO_6$: 383.1, found: 383.1.



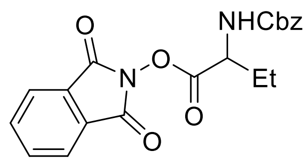
1,3-Dioxoisoindolin-2-yl 2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)butanoate. The title compound was synthesized according to **GP-3** from 2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)butanoic acid (5.00 g, 15.4 mmol). 4.60 g (9.79 mmol, 64% yield). White solid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.85 (m, 2H), 7.85 – 7.72 (m, 4H), 7.64 – 7.57 (m, 2H), 7.43 – 7.37 (m, 2H), 7.36 – 7.29 (m, 2H), 5.32 (d, *J* = 8.6 Hz, 1H), 4.84 – 4.59 (m, 1H), 4.52 – 4.43 (m, 2H), 4.25 (t, *J* = 7.0 Hz, 1H), 2.21 – 1.89 (m, 2H), 1.12 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 161.6, 155.7, 143.9, 143.7, 141.4, 135.0, 128.9, 127.8, 127.2, 125.2, 124.2, 120.1, 67.4, 53.6, 47.2, 26.3, 9.4.

FT-IR (film): 3340, 2974, 1789, 1745, 1518, 1186, 1065, 758, 696 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{27}H_{22}N_2NaO_6$: 493.1, found: 493.1.



1,3-Dioxoisoindolin-2-yl 2-(((benzyloxy)carbonyl)amino)butanoate. The title compound was synthesized according to **GP-3** from 2-(((benzyloxy)carbonyl)amino)butanoic acid (3.60 g, 15.2 mmol). 2.46 g (6.44 mmol, 42% yield). White solid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.86 – 7.75 (m, 2H), 7.40 – 7.28 (m, 5H), 5.34 – 5.27 (m, 1H), 5.21 – 5.09 (m, 2H), 4.86 – 4.54 (m, 1H), 2.19 – 1.90 (m, 2H), 1.11 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 161.6, 155.7, 136.1, 135.0, 128.9, 128.7, 128.4, 128.3, 124.2, 67.5, 53.5, 26.4, 9.3.

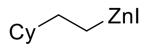
FT-IR (film): 3328, 1788, 1745, 1186, 1065, 877, 696 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{20}H_{18}N_2NaO_6$: 405.1, found: 405.1.

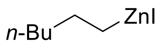
IV. Preparation of Nucleophiles

$$\mathrm{R{-}I} \xrightarrow[\text{THF, 50 °C}]{\mathrm{Zn,\ I_2}} \mathrm{R{-}ZnI}$$

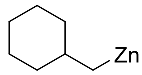
General Procedure 4 (GP-4): Preparation of organozinc reagents. In the air, an oven-dried 100 mL Schlenk tube was charged with a stir bar and zinc powder (1.5 equiv, ~100 mesh, Alfa, 99.9%), and then it was sealed with a rubber septum cap. The tube was placed under a nitrogen atmosphere by evacuating and back-filling the tube (three cycles). Then, the tube was heated with a heat gun (~250 °C) under vacuum (~1 torr) for 10 min. The Schlenk tube was allowed to cool to room temperature, and it was back-filled with nitrogen. THF (0.5 mL/mmol of the alkyl iodide) was added via syringe. The cap was removed, and iodine (0.050 equiv) was added in one portion under a positive flow of nitrogen (the cap was then replaced), leading initially to a red color that faded after ~5 sec of vigorous stirring (1000 rpm). A solution of the alkyl iodide (1.0 equiv) in THF (0.5 mL/mmol of the alkyl iodide), prepared in a 20 mL vial equipped with a nitrogen balloon, was added via syringe in one portion to the gray suspension of zinc powder. Then, the Schlenk tube was capped tightly under a nitrogen atmosphere and transferred to an oil bath. The reaction mixture was stirred vigorously at 50 °C for 12 h (the disappearance of the alkyl iodide and the formation of the alkylzinc reagent can readily be monitored via GC analysis of the quenched alkylzinc reagent). After the alkyl iodide had been consumed, the gray mixture was filtered through a syringe filter (PTFE, 0.45 μM) to afford a colorless to slightly yellow solution. The alkylzinc solution was titrated by the method of Knochel, using iodine in THF.[4] The concentration of the alkylzinc reagents remained constant over one year when stored at room temperature in a glovebox.



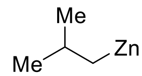
Zn-1
[0.98 M]



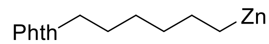
Zn-2
[1.02 M]



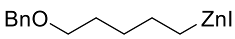
Zn-3
[1.10 M]



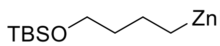
Zn-4
[0.95 M]



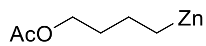
Zn-5
[0.92 M]



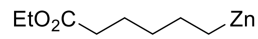
Zn-6
[0.95 M]



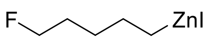
Zn-7
[0.89 M]



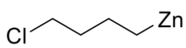
Zn-8
[0.98 M]



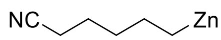
Zn-9
[1.00 M]



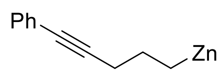
Zn-10
[1.06 M]



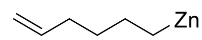
Zn-11
[1.12 M]



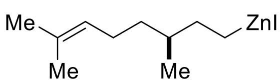
Zn-12
[0.95 M]



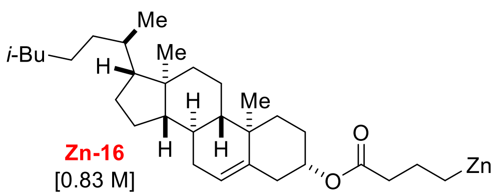
Zn-13
[0.95 M]



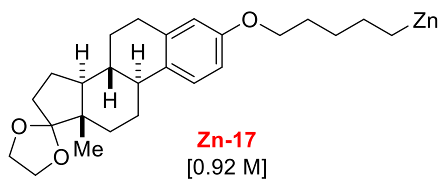
Zn-14
[1.03 M]



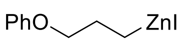
Zn-15
[0.99 M]



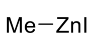
Zn-16
[0.83 M]



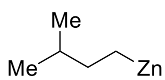
Zn-17
[0.92 M]



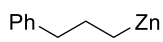
Zn-18
[1.00 M]



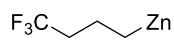
Zn-19
[0.98 M]



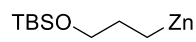
Zn-20
[1.05 M]



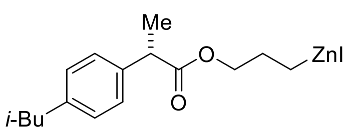
Zn-21
[1.05 M]



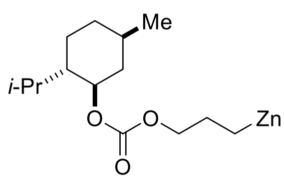
Zn-22
[1.02 M]



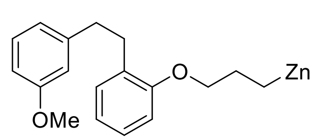
Zn-23
[0.96 M]



Zn-24
[0.85 M]

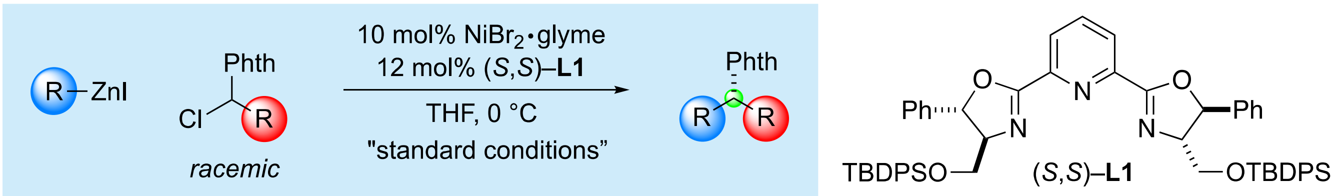


Zn-25
[0.75 M]



Zn-26
[0.98 M]

V. Catalytic Enantioconvergent Cross-Couplings

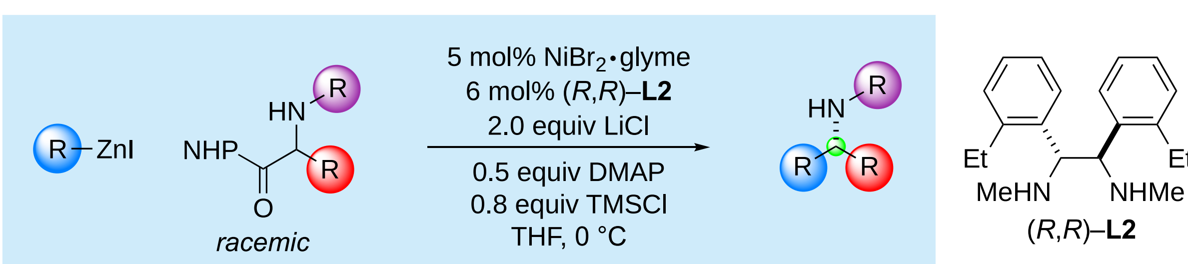


General Procedure 5 (GP-5): Alkyl chlorides as the electrophile.

Preparation of a solution of the catalyst: In the air, $NiBr_2$·glyme (18.4 mg, 0.060 mmol, 10 mol%) and (*S*,*S*)-**L1** (65.2 mg, 0.072 mmol, 12 mol%) were added to an oven-dried 40 mL vial equipped with a cross-type stir bar. The vial was closed with a PTFE septum cap, the joint was wrapped with electric tape, and the vial was placed under a nitrogen atmosphere by evacuating and back-filling the vial (three cycles). A balloon filled with nitrogen was attached to the vial. THF (6.0 mL) was added to the vial, and the mixture was stirred at room temperature for 30 min, leading to an orange, homogeneous solution.

Cross-coupling: In the air, an oven-dried 8 mL vial was charged with the racemic alkyl chloride (0.60 mmol, 1.0 equiv). The vial was closed with a PTFE septum cap, and then it was evacuated and back-filled with nitrogen (three cycles). THF (3.0 mL) was added, and the resulting solution was transferred via syringe to the 40 mL reaction vial. The 8 mL vial was rinsed with THF (3.0 mL), and the washing was transferred to the reaction vial. The reaction vial was then placed in an *i*-PrOH cooling bath at 0 °C, and the reaction mixture was stirred at 0 °C for 10 min. Then, the alkylzinc solution (0.66 mmol, 1.1 equiv) was added dropwise via syringe over 3 min, during which the reaction mixture turned dark. The balloon was removed, and the septum cap was sealed with grease. The mixture was stirred at 0 °C for 36 h.

Work-up: The reaction was quenched with methanol (0.2 mL), and the mixture was passed through a plug of silica gel; the vial, the cap, and the silica gel were rinsed with Et_2O. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel.



General Procedure 6 (GP-6): NHP esters as the electrophile.

Preparation of a solution of the catalyst: In the air, $NiBr_2$·glyme (9.3 mg, 0.030 mmol, 5.0 mol%), (*R*,*R*)-**L2** (10.7 mg, 0.036 mmol, 6.0 mol%), and anhydrous LiCl (52.1 mg, 1.2 mmol, 2.0 equiv; because LiCl is hygroscopic, it is recommended to weigh the compound in a capped 4 mL vial in a glovebox, transfer the vial out of the glovebox, and pour the compound into the reaction vial) were added sequentially to an oven-dried 40 mL vial equipped with a cross-type stir bar. The vial was then capped with a PTFE septum cap and wrapped with electrical tape. The reaction vial was evacuated and back-filled with nitrogen (four cycles), after which a nitrogen-filled balloon was attached. THF (4.5 mL) was added via syringe, and the mixture was allowed to stir for 30 min, during which it became a light-green, homogeneous solution.

Cross-coupling: In the air, an oven-dried 8 mL vial was charged with DMAP (36.7 mg, 0.30 mmol, 0.50 equiv) and the NHP ester (0.60 mmol, 1.0 equiv). The vial was closed with a PTFE septum cap, and then it was evacuated and back-filled with nitrogen (three cycles). THF (3.0 mL) was added, and the resulting solution was transferred via syringe to the 40 mL reaction vial, leading to an orange, opaque mixture. The 8 mL vial was rinsed with THF (0.5 mL), which was also added to the reaction vial. Next, TMSCl (61 μL, 0.48 mmol, 0.80 equiv) was added via microsyringe, leading to a colorless, opaque mixture. The reaction vial was then placed in an *i*-PrOH cooling bath at 0 °C, and the mixture was stirred at 0 °C for 10 min. Then, the alkylzinc solution (0.72 mmol, 1.2 equiv) was added dropwise via syringe over 5 min, during which the reaction mixture became yellow and homogeneous. The balloon was removed and the septum cap was sealed with grease. The mixture was stirred at 0 °C for 18 h.

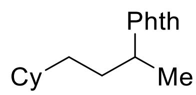
Work-up: The reaction was quenched with methanol (0.2 mL), and the mixture was passed through a plug of silica gel; the vial, the cap, and the silica gel were rinsed with Et_2O. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel.

General Procedure 7 (GP-7): α-branched NHP esters as the electrophile.

Preparation of a solution of the catalyst: In the air, $NiBr_2$·glyme (18.6 mg, 0.060 mmol, 10 mol%), (*R*,*R*)-**L2** (21.4 mg, 0.072 mmol, 12 mol%), and anhydrous LiCl (130 mg, 3.0 mmol, 5.0 equiv; because LiCl is hygroscopic, it is recommended to weigh the compound in a capped 4 mL vial in a glovebox, transfer the vial out of the glovebox, and pour the compound into the reaction vial) were added sequentially to an oven-dried 40 mL vial equipped with a cross-type stir bar. The vial was then capped with a PTFE septum cap and wrapped with electrical tape. The reaction vial was evacuated and back-filled with nitrogen (four cycles), after which a nitrogen-filled balloon was attached. THF (4.5 mL) was added via syringe, and the mixture was allowed to stir for 30 min, during which it became a light-green, homogeneous solution.

Cross-coupling: In the air, an oven-dried 8 mL vial was charged with the NHP ester (0.60 mmol, 1.0 equiv). The vial was closed with a PTFE septum cap, and then it was evacuated and back-filled with nitrogen (three cycles). THF (3.0 mL) was added, and the resulting solution was transferred via syringe to the 40 mL reaction vial, leading to an orange, homogeneous solution. The 8 mL vial was rinsed with THF (0.5 mL), which was also added to the reaction vial. The reaction vial was then placed in an *i*-PrOH cooling bath at 0 °C, and the mixture was stirred at 0 °C for 10 min. Then, the alkylzinc solution (0.72 mmol, 1.2 equiv) was added dropwise via syringe over 5 min, during which the reaction mixture became lightred and homogeneous. The balloon was removed, and the septum cap was sealed with grease. The mixture was stirred at 0 °C for 18 h.

Work-up: The reaction was quenched with methanol (0.2 mL), and the mixture was passed through a plug of silica gel; the vial, the cap, and the silica gel were rinsed with Et_2O. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel.



2-(4-Cyclohexylbutan-2-yl)isoindoline-1,3-dione (1). The title compound was synthesized according to **GP-5** from 2-(1-chloroethyl)isoindoline-1,3-dione and **Zn-1**. The product was purified by column chromatography on silica gel (1:10 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 159 mg, 93% yield, 88% ee; (*R*,*R*)-**L1**: 164 mg, 96% yield, 88% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 3.9 min (minor), 4.9 min (major).

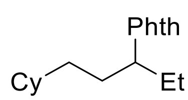
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.73 – 7.66 (m, 2H), 4.35 – 4.23 (m, 1H), 2.12 – 1.97 (m, 1H), 1.82 – 1.69 (m, 1H), 1.68 – 1.55 (m, 5H), 1.45 (d, J = 6.9 Hz, 3H), 1.29 – 0.99 (m, 6H), 0.91 – 0.73 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 133.9, 132.2, 123.2, 48.0, 37.6, 34.6, 33.5, 33.3, 31.3, 26.7, 26.5, 26.4, 18.9.

FT-IR (film): 3470, 2920, 2353, 1697, 1367, 1022, 869, 728 cm^{-1}.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{18}H_{24}NO_2$: 286.1802, found: 286.1806.

$[\alpha]^{22}_D = -13.3$ (c 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L1**.



2-(1-Cyclohexylpentan-3-yl)isoindoline-1,3-dione (2). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-1**. The product was purified by column chromatography on silica gel (1:15 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 167 mg, 93% yield, 92% ee; (*R*,*R*)-**L1**: 171 mg, 95% yield, 92% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 3.8 min (minor), 4.1 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.73 – 7.67 (m, 2H), 4.12 – 4.01 (m, 1H), 2.13 – 1.97 (m, 2H), 1.84 – 1.68 (m, 2H), 1.68 – 1.55 (m, 5H), 1.26 – 0.99 (m, 6H), 0.85 (t, J = 7.6 Hz, 3H), 0.87 – 0.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 133.9, 132.0, 123.2, 54.5, 37.6, 34.5, 33.6, 33.3, 29.7, 26.7, 26.5, 26.4, 25.7, 11.3.

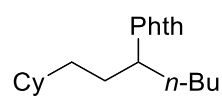
FT-IR (film): 3466, 2916, 2353, 1697, 1362, 1050, 727 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{19}H_{26}NO_2$: 300.1958, found: 300.1962.

$[\alpha]^{22}_D = -5.2$ (*c* 1.0, $CHCl_3$); 92% ee, from (*S*,*S*)-**L1**.

Gram-scale reaction: In the air, $NiBr_2$·glyme (153 mg, 0.50 mmol, 0.10 equiv) and (*S*,*S*)-**L1** (543 mg, 0.60 mmol, 0.12 equiv) were added to an oven-dried 250 mL round-bottom flask equipped with a stir bar. The flask was closed with a rubber septum cap, the joint was wrapped with electrical tape, and the flask was placed under a nitrogen atmosphere by evacuating and back-filling the flask (three cycles). A balloon filled with nitrogen was attached to the reaction flask. THF (40 mL) was added to the flask, and the mixture was stirred at room temperature for 30 min, at which time it was an orange, homogeneous solution. In the air, an oven-dried 40 mL vial was charged with 2-(1-chloropropyl)isoindoline-1,3-dione (1.12 g, 5.0 mmol, 1.0 equiv). The vial was capped with a PTFE septum cap, and then it was evacuated and back-filled with nitrogen (three cycles). THF (30 mL) was added to the vial to dissolve the electrophile. Next, this solution of the electrophile was added in one portion via syringe to the catalyst solution. The 40 mL vial was rinsed with THF (30 mL), and the washing was transferred to the reaction flask. The reaction flask was then placed in an *i*-PrOH cooling bath at 0 °C, and the reaction mixture was stirred at 0 °C for 10 min. Then, **Zn-1** (5.5 mmol, 1.1 equiv) was added dropwise via syringe over 10 min, during which the reaction mixture turned dark. The balloon was removed, and the septum was sealed with electrical tape. The reaction mixture was stirred at 0 °C for 36 h. The reaction was quenched at 0 °C by the addition of MeOH (1.0 mL). Next, the reaction mixture was passed through a column of silica gel (5 cm), and the flask, the septum, and the silica gel were rinsed with Et_2O. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (1:15 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 1.40 g, 93% yield, 92% ee.



2-(1-Cyclohexylheptan-3-yl)isoindoline-1,3-dione (3). The title compound was synthesized according to **GP-5** from 2-(1-chloropentyl)isoindoline-1,3-dione and **Zn-1**. The product was purified by column chromatography on silica gel (1:15 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 189 mg, 96% yield, 91% ee; (*R*,*R*)-**L1**: 183 mg, 93% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 10.4 min (minor), 11.3 min (major).

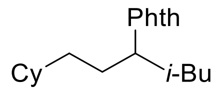
^1H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.74 – 7.67 (m, 2H), 4.19 – 4.08 (m, 1H), 2.13 – 1.98 (m, 2H), 1.78 – 1.54 (m, 7H), 1.40 – 0.98 (m, 10H), 0.91 – 0.72 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 133.9, 132.0, 123.2, 52.8, 37.6, 34.5, 33.6, 33.3, 32.4, 30.0, 29.0, 26.8, 26.5, 26.4, 22.5, 14.1.

FT-IR (film): 3466, 2919, 2354, 1699, 1371, 1050, 876, 726 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{21}H_{30}NO_2$: 328.2271, found: 328.2268.

$[\alpha]^{22}_D = -1.7$ (*c* 1.0, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



2-(1-Cyclohexyl-5-methylhexan-3-yl)isoindoline-1,3-dione (4). The title compound was synthesized according to **GP-5** from 2-(1-chloro-3-methylbutyl)isoindoline-1,3-dione and **Zn-1**. The product was purified by column chromatography on silica gel (1:12 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 175 mg, 89% yield, 81% ee; (*R*,*R*)-**L1**: 176 mg, 90% yield, 81% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IE-3 column (3% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 4.7 min (minor), 4.9 min (major).

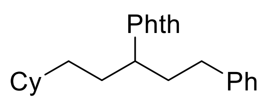
^1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.75 (m, 2H), 7.75 – 7.64 (m, 2H), 4.33 – 4.16 (m, 1H), 2.25 – 1.94 (m, 2H), 1.75 – 1.55 (m, 6H), 1.50 – 1.36 (m, 2H), 1.27 – 0.98 (m, 6H), 0.96 – 0.73 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 133.9, 132.0, 123.2, 50.8, 41.6, 37.7, 34.5, 33.5, 33.3, 30.4, 26.8, 26.5, 26.4, 25.4, 23.4, 22.0.

FT-IR (film): 3464, 2919, 2354, 1709, 1372, 1168, 1072, 871, 720 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{21}H_{30}NO_2$: 328.2271, found: 328.2269.

$[\alpha]^{22}_D = -2.8$ (*c* 1.0, $CHCl_3$); 81% ee, from (*S*,*S*)-**L1**.



2-(1-Cyclohexyl-5-phenylpentan-3-yl)isoindoline-1,3-dione (5). The title compound was synthesized according to **GP-5** from 2-(1-chloro-3-phenylpropyl)isoindoline-1,3-dione and **Zn-1**. The product was purified by column chromatography on silica gel (1:15 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 219 mg, 97% yield, 90% ee; (*R*,*R*)-**L1**: 223 mg, 99% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 7.1 min (minor), 7.4 min (major).

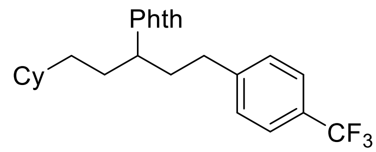
^1H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 2H), 7.74 – 7.65 (m, 2H), 7.22 – 7.15 (m, 2H), 7.15 – 7.09 (m, 2H), 7.09 – 7.03 (m, 1H), 4.27 – 4.16 (m, 1H), 2.69 – 2.43 (m, 3H), 2.15 – 1.94 (m, 2H), 1.82 – 1.69 (m, 1H), 1.69 – 1.54 (m, 5H), 1.25 – 1.01 (m, 6H), 0.91 – 0.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 141.4, 133.9, 131.9, 128.4, 125.9, 123.2, 52.7, 37.6, 34.3, 34.0, 33.5, 33.34, 33.29, 30.1, 26.7, 26.5, 26.4.

FT-IR (film): 3464, 2920, 2353, 1708, 1378, 1077, 885 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{25}H_{30}NO_2$: 376.2271, found: 376.2277.

$[\alpha]^{22}_D = -9.1$ (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



2-(1-Cyclohexyl-5-(4-(trifluoromethyl)phenyl)pentan-3-yl)isoindoline-1,3-dione (6). The title compound was synthesized according to **GP-5** from 2-(1-chloro-3-(4-(trifluoromethyl)phenyl)propyl)isoindoline-1,3-dione and **Zn-1**. The product was purified by column chromatography on silica gel (1:12 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 259 mg, 97% yield, 88% ee; (*R*,*R*)-**L1**: 250 mg, 94% yield, 88% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 7.2 min (minor), 7.5 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 2H), 7.71 – 7.63 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.26 – 4.15 (m, 1H), 2.79 – 2.66 (m, 1H), 2.66 – 2.49 (m, 2H), 2.15 – 1.94 (m, 2H), 1.82 – 1.68 (m, 1H), 1.68 – 1.53 (m, 5H), 1.23 – 0.97 (m, 6H), 0.90 – 0.70 (m, 2H).

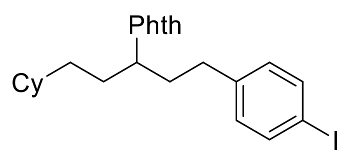
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 145.4 (q, *J* = 1.0 Hz), 134.0, 131.8, 128.7, 128.2 (q, *J* = 32.3 Hz), 125.2 (q, *J* = 4.0 Hz), 124.3 (q, *J* = 273 Hz), 123.1, 52.6, 37.5, 34.3, 33.5, 33.34, 33.29, 33.27, 30.2, 26.7, 26.43, 26.38.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.3.

FT-IR (film): 3466, 2920, 2354, 1710, 1366, 1120, 1019, 847, 719 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{26}H_{29}F_3NO_2$: 444.2145, found: 444.2145.

$[\alpha]^{22}_{D}$ = –13.2 (*c* 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L1**.



2-(1-Cyclohexyl-5-(4-iodophenyl)pentan-3-yl)isoindoline-1,3-dione (7). The title compound was synthesized according to **GP-5** from 2-(1-chloro-3-(4-iodophenyl)propyl)isoindoline-1,3-dione and **Zn-1**. The product was purified by column chromatography on silica gel (1:15 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 257 mg, 85% yield, 89% ee; (*R*,*R*)-**L1**: 247 mg, 82% yield, 88% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OJ-3 column (10% CH_3CN in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 5.9 min (major), 6.7 min (minor).

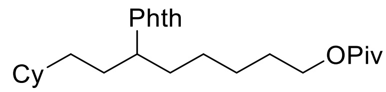
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.74 – 7.66 (m, 2H), 7.49 – 7.40 (m, 2H), 6.90 – 6.81 (m, 2H), 4.24 – 4.11 (m, 1H), 2.67 – 2.42 (m, 3H), 2.15 – 1.89 (m, 2H), 1.78 – 1.58 (m, 6H), 1.29 – 0.97 (m, 6H), 0.91 – 0.70 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 141.0, 137.4, 134.1, 131.8, 130.5, 123.2, 90.9, 52.6, 37.5, 34.3, 33.5, 33.4, 33.3, 33.0, 30.2, 26.7, 26.5, 26.4.

FT-IR (film): 3454, 2915, 2352, 1700, 1358, 1006, 720 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{25}H_{29}INO_2$: 502.1237, found: 502.1229.

$[\alpha]^{22}_{D}$ = −15.2 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L1**.



8-Cyclohexyl-6-(1,3-dioxoisoindolin-2-yl)octyl pivalate (8). The title compound was synthesized according to **GP-5** from 6-chloro-6-(1,3-dioxoisoindolin-2-yl)hexyl pivalate and **Zn-1**. The product was purified by column chromatography on silica gel (1:5 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 241 mg, 91% yield, 90% ee; (*R*,*R*)-**L1**: 244 mg, 92% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 7.7 min (minor), 8.0 min (major).

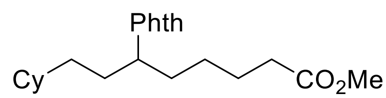
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 2H), 7.76 – 7.64 (m, 2H), 4.22 – 4.06 (m, 1H), 3.99 (t, *J* = 6.5 Hz, 2H), 2.15 – 1.98 (m, 2H), 1.78 – 1.51 (m, 9H), 1.45 – 0.97 (m, 19H), 0.90 – 0.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 168.9, 134.0, 132.0, 123.3, 64.4, 52.7, 38.8, 37.6, 34.4, 33.5, 33.3, 32.6, 30.0, 28.7, 27.3, 26.7, 26.52, 26.46, 26.4, 25.9.

FT-IR (film): 3469, 2918, 2354, 1713, 1370, 1049, 870, 720 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{27}H_{40}NO_4$: 442.2952, found: 442.2960.

$[\alpha]^{22}_{D}$ = +0.7 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



Methyl 8-cyclohexyl-6-(1,3-dioxoisoindolin-2-yl)octanoate (9). The title compound was synthesized according to **GP-5** from methyl 6-chloro-6-(1,3-dioxoisoindolin-2-yl)hexanoate and **Zn-1**. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 209 mg, 91% yield, 91% ee; (*R*,*R*)-**L1**: 210 mg, 91% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 11.9 min (minor), 13.0 min (major).

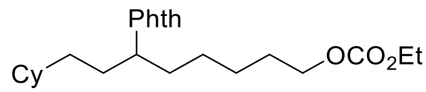
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.74 – 7.67 (m, 2H), 4.19 – 4.09 (m, 1H), 3.61 (s, 3H), 2.25 (t, *J* = 7.7 Hz, 2H), 2.16 – 1.98 (m, 2H), 1.78 – 1.57 (m, 9H), 1.36 – 0.98 (m, 8H), 0.89 – 0.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 168.9, 134.0, 132.0, 123.3, 52.6, 51.6, 37.6, 34.4, 34.0, 33.6, 33.3, 32.3, 30.0, 26.7, 26.5, 26.4, 26.3, 24.7.

FT-IR (film): 3463, 2913, 2355, 1698, 1050, 737 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{23}H_{35}N_2O_4$: 403.2591, found: 403.2588.

$[\alpha]^{22}_{D}$ = +1.4 (*c* 1.0, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



8-Cyclohexyl-6-(1,3-dioxoisoindolin-2-yl)octyl ethyl carbonate (10). The title compound was synthesized according to **GP-5** from 6-chloro-6-(1,3-dioxoisoindolin-2-yl)hexyl ethyl carbonate and **Zn-1**. The product was purified by column chromatography on silica gel (1:3 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 218 mg, 85% yield, 90% ee; (*R*,*R*)-**L1**: 225 mg, 87% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 8.8 min (minor), 9.2 min (major).

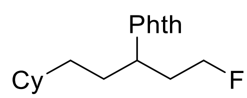
^1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 2H), 7.76 – 7.65 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.17 – 4.09 (m, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.17 – 1.94 (m, 2H), 1.76 – 1.56 (m, 9H), 1.47 – 0.97 (m, 13H), 0.90 – 0.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) 168.9, 155.4, 134.0, 131.9, 123.3, 67.9, 63.9, 52.7, 37.6, 34.4, 33.5, 33.3, 32.5, 30.0, 28.7, 26.7, 26.5, 26.44, 26.41, 25.6, 14.4.

FT-IR (film): 3464, 2920, 2354, 1711, 1168, 1046, 726 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{36}NO_5$: 430.2588, found: 430.2584.

$[\alpha]^{22}_D$ = +0.8 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



2-(1-Cyclohexyl-5-fluoropentan-3-yl)isoindoline-1,3-dione (11). The title compound was synthesized according to **GP-5** from 2-(1-chloro-3-fluoropropyl)isoindoline-1,3-dione and **Zn-1**. The product was purified by column chromatography on silica gel (1:6 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 141 mg, 74% yield, 88% ee; (*R*,*R*)-**L1**: 142 mg, 75% yield, 88% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 3.7 min (minor), 4.0 min (major).

^1H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 2H), 7.77 – 7.65 (m, 2H), 4.58 – 4.28 (m, 3H), 2.60 – 2.39 (m, 1H), 2.22 – 2.02 (m, 2H), 1.86 – 1.70 (m, 1H), 1.69 – 1.58 (m, 5H), 1.31 – 0.99 (m, 6H), 0.93 – 0.70 (m, 2H).

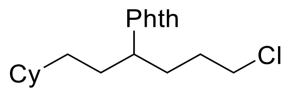
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 134.1, 131.9, 123.4, 81.7 (d, *J* = 167 Hz), 49.3 (d, *J* = 4.0 Hz), 37.5, 34.2, 33.5, 33.3, 33.2 (d, *J* = 19.2 Hz), 29.9, 26.7, 26.5, 26.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ –220.8.

FT-IR (film): 3469, 2920, 2356, 1713, 1372, 1066, 873, 720 cm^{-1}.

LC-MS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{19}H_{25}FNO_2$: 318.2, found: 318.2.

$[\alpha]^{22}_D$ = +7.8 (*c* 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L1**.



2-(6-Chloro-1-cyclohexylhexan-3-yl)isoindoline-1,3-dione (12). The title compound was synthesized according to **GP-5** from 2-(1,4-dichlorobutyl)isoindoline-1,3-dione and **Zn-1**. The product was purified by column chromatography on silica gel (1:8 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 204 mg, 98% yield, 90% ee; (*R*,*R*)-**L1**: 194 mg, 93% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 8.2 min (minor), 8.5 min (major).

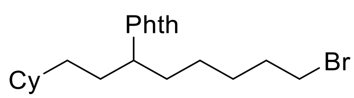
^1H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.78 (m, 2H), 7.78 – 7.65 (m, 2H), 4.26 – 4.09 (m, 1H), 3.62 – 3.45 (m, 2H), 2.29 – 2.15 (m, 1H), 2.15 – 2.01 (m, 1H), 1.96 – 1.84 (m, 1H), 1.81 – 1.68 (m, 3H), 1.68 – 1.57 (m, 5H), 1.28 – 0.98 (m, 6H), 0.91 – 0.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 134.1, 131.9, 123.4, 52.0, 44.5, 37.6, 34.4, 33.5, 33.3, 30.0, 29.9, 29.8, 26.7, 26.5, 26.4.

FT-IR (film): 3466, 2356, 1707, 1367, 1051, 871, 722 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{27}ClNO_2$: 348.1725, found: 348.1730.

$[\alpha]^{22}_D$ = +0.6 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



2-(8-Bromo-1-cyclohexyloctan-3-yl)isoindoline-1,3-dione (13). The title compound was synthesized according to **GP-5** from 2-(6-bromo-1-chlorohexyl)isoindoline-1,3-dione and **Zn-1**. The product was purified by column chromatography on silica gel (1:12 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 220 mg, 87% yield, 91% ee; (*R*,*R*)-**L1**: 215 mg, 86% yield, 91% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 13.0 min (minor), 13.9 min (major).

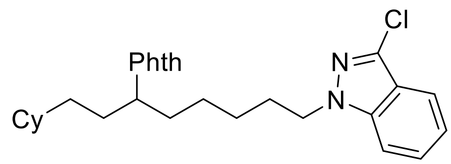
^1H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 2H), 7.77 – 7.63 (m, 2H), 4.25 – 4.05 (m, 1H), 3.35 (t, *J* = 6.8 Hz, 2H), 2.20 – 1.98 (m, 2H), 1.85 – 1.76 (m, 2H), 1.76 – 1.56 (m, 7H), 1.52 – 1.34 (m, 2H), 1.35 – 1.00 (m, 8H), 0.90 – 0.73 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 134.0, 132.0, 123.3, 52.6, 37.6, 34.5, 33.9, 33.6, 33.3, 32.7, 32.5, 30.0, 28.0, 26.7, 26.5, 26.4, 26.0.

FT-IR (film): 3465, 2354, 1704, 1379, 1047, 868, 722 cm^{-1}.

LC-MS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{31}BrNO_2$: 420.2, found: 420.1.

$[\alpha]^{22}_D$ = +4.4 (*c* 1.0, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



2-(8-(3-Chloro-1*H*-indazol-1-yl)-1-cyclohexyloctan-3-yl)isoindoline-1,3-dione (14). The title compound was synthesized according to **GP-5** from 2-(1-chloro-6-(3-chloro-1*H*-indazol-1-yl)hexyl)isoindoline-1,3-dione and **Zn-1**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 249 mg, 84% yield, 88% ee; (*R*,*R*)-**L1**: 249 mg, 84% yield, 87% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK ID-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 5.9 min (minor), 6.2 min (major).

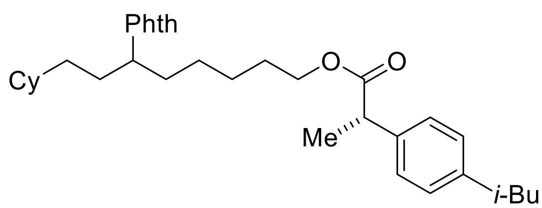
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.74 – 7.67 (m, 2H), 7.64 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.32 (dt, *J* = 8.6, 1.0 Hz, 1H), 7.20 – 7.12 (m, 1H), 4.25 (t, *J* = 7.1 Hz, 2H), 4.16 – 4.05 (m, 1H), 2.12 – 1.96 (m, 2H), 1.92 – 1.78 (m, 2H), 1.71 – 1.54 (m, 7H), 1.41 – 0.96 (m, 10H), 0.89 – 0.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 140.9, 134.0, 132.6, 131.9, 127.4, 123.3, 121.14, 121.06, 119.9, 109.4, 52.6, 49.2, 37.6, 34.4, 33.5, 33.3, 32.4, 30.0, 29.8, 26.7, 26.6, 26.5, 26.41, 26.38.

FT-IR (film): 3468, 2353, 1709, 1365, 1049, 873, 728, 682 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{29}H_{35}ClN_3O_2$: 492.2412, found: 492.2420.

$[\alpha]^{22}_D$ = +3.3 (*c* 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L1**.



8-Cyclohexyl-6-(1,3-dioxoisoindolin-2-yl)octyl (2*S*)-2-(4-isobutylphenyl)propanoate (15, 16). The title compound was synthesized according to **GP-5** from 6-chloro-6-(1,3-dioxoisoindolin-2-yl)hexyl (2*S*)-2-(4-isobutylphenyl)propanoate and **Zn-1**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 279 mg, 85% yield, 95:5 d.r.; (*R*,*R*)-**L1**: 287 mg, 88% yield, 5:95 d.r.

SFC analysis: The d.r. was determined via SFC on a CHIRALPAK IG-3 column (10% MeOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 9.8 min (minor), 12.4 min (major).

NMR data for the product from (*S*,*S*)-**L1**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.74 – 7.67 (m, 2H), 7.20 – 7.14 (m, 2H), 7.10 – 7.04 (m, 2H), 4.17 – 4.06 (m, 1H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.64 (q, *J* = 7.1 Hz, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 2.12 – 1.96 (m, 2H), 1.89 – 1.76 (m, 1H), 1.75 – 1.59 (m, 7H), 1.55 – 1.48 (m, 2H), 1.45 (d, *J* = 7.2 Hz, 3H), 1.33 – 0.98 (m, 10H), 0.88 (d, *J* = 6.6 Hz, 6H), 0.86 – 0.73 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 168.9, 140.6, 138.0, 134.0, 132.0, 129.4, 127.3, 123.3, 64.7, 52.7, 45.3, 45.2, 37.6, 34.5, 33.6, 33.3, 32.5, 30.3, 30.0, 28.5, 26.7, 26.5, 26.4, 25.7, 22.5, 18.6.

NMR data for the product from (*R*,*R*)-**L1**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.74 – 7.67 (m, 2H), 7.21 – 7.14 (m, 2H), 7.11 – 7.04 (m, 2H), 4.17 – 4.07 (m, 1H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.65 (q, *J* = 7.2 Hz, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 2.12 – 1.97 (m, 2H), 1.89 – 1.77 (m, 1H), 1.72 – 1.58 (m, 7H), 1.56 – 1.48 (m, 2H), 1.45 (d, *J* = 7.2 Hz, 3H), 1.33 – 0.98 (m, 10H), 0.88 (d, *J* = 6.6 Hz, 6H), 0.86 – 0.73 (m, 2H).

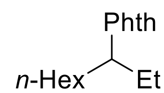
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 168.9, 140.6, 138.0, 134.0, 132.0, 129.4, 127.3, 123.3, 64.7, 52.7, 45.3, 45.2, 37.6, 34.5, 33.6, 33.3, 32.5, 30.3, 30.0, 28.5, 26.7, 26.5, 26.4, 25.7, 22.5, 18.6.

FT-IR (film): 3468, 2919, 2354, 1710, 1030, 682 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{35}H_{48}NO_4$: 546.3578, found: 546.3576.

$[\alpha]^{22}_{D}$ = +16.9 (*c* 1.0, $CHCl_3$); 95:5 d.r., from (*S*,*S*)-**L1**.

$[\alpha]^{22}_{D}$ = +14.9 (*c* 1.0, $CHCl_3$); 5:95 d.r., from (*R*,*R*)-**L1**.



2-(Nonan-3-yl)isoindoline-1,3-dione (17). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-2**. The product was purified by column chromatography on silica gel (1:10 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 153 mg, 93% yield, 89% ee; (*R*,*R*)-**L1**: 153 mg, 93% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IF-3 column (2% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 5.3 min (minor), 5.8 min (major).

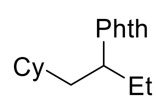
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.73 – 7.67 (m, 2H), 4.16 – 4.05 (m, 1H), 2.13 – 1.98 (m, 2H), 1.83 – 1.65 (m, 2H), 1.35 – 1.14 (m, 8H), 0.90 – 0.78 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 133.9, 132.0, 123.2, 54.1, 32.4, 31.8, 29.1, 26.8, 25.7, 22.7, 14.2, 11.3.

FT-IR (film): 3464, 2921, 2364, 1714, 1360, 1041, 796, 720 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{17}H_{24}NO_2$: 274.1802, found: 274.1807.

$[\alpha]^{22}_{D}$ = –6.1 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L1**.



2-(1-Cyclohexylbutan-2-yl)isoindoline-1,3-dione (18). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-3**. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 163 mg, 95% yield, 95% ee; (*R*,*R*)-**L1**: 167 mg, 98% yield, 95% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 4.4 min (minor), 4.9 min (major).

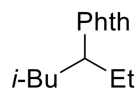
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.73 – 7.66 (m, 2H), 4.29 – 4.19 (m, 1H), 2.13 – 1.96 (m, 2H), 1.91 – 1.80 (m, 1H), 1.78 – 1.44 (m, 6H), 1.20 – 1.05 (m, 4H), 0.99 – 0.78 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 133.9, 132.0, 123.2, 51.3, 39.9, 34.8, 33.9, 32.7, 26.6, 26.4, 26.2, 26.1, 11.3.

FT-IR (film): 3463, 2924, 2356, 1708, 1371, 1064, 886, 720 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{18}H_{24}NO_2$: 286.1802, found: 286.1806.

$[\alpha]^{22}_{D}$ = –18.0 (*c* 1.0, $CHCl_3$); 95% ee, from (*S*,*S*)-**L1**.



2-(5-Methylhexan-3-yl)isoindoline-1,3-dione (19). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-4**. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 133 mg, 90% yield, 94% ee; (*R*,*R*)-**L1**: 135 mg, 92% yield, 93% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (2% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 4.3 min (minor), 4.5 min (major).

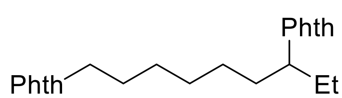
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.73 – 7.66 (m, 2H), 4.27 – 4.17 (m, 1H), 2.20 – 1.97 (m, 2H), 1.80 – 1.66 (m, 1H), 1.50 – 1.38 (m, 2H), 0.95 – 0.82 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 133.9, 132.0, 123.2, 52.0, 41.3, 26.1, 25.4, 23.4, 21.9, 11.3.

FT-IR (film): 3460, 2956, 2354, 1770, 1470, 1336, 1174, 1062, 867, 720 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{15}H_{20}NO_2$: 246.1489, found: 246.1490.

$[\alpha]^{22}_{D}$ = +1.3 (*c* 1.0, $CHCl_3$); 94% ee, from (*S*,*S*)-**L1**.



2,2'-(Nonane-1,7-diyl)bis(isoindoline-1,3-dione) (20). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-5**. The product was purified by column chromatography on silica gel (1:2 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 238 mg, 95% yield, 91% ee; (*R*,*R*)-**L1**: 230 mg, 92% yield, 92% ee.

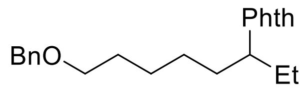
SFC analysis: The ee was determined via SFC on a CHIRALPAK ID-3 column (35% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 9.5 min (minor), 12.3 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 4H), 7.74 – 7.65 (m, 4H), 4.14 – 4.03 (m, 1H), 3.63 (t, *J* = 7.3 Hz, 2H), 2.14 – 1.96 (m, 2H), 1.83 – 1.66 (m, 2H), 1.64 – 1.56 (m, 2H), 1.41 – 1.16 (m, 6H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 168.6, 133.9, 133.9, 132.3, 132.0, 123.3, 123.2, 54.0, 38.1, 32.3, 29.0, 28.7, 26.9, 26.7, 25.7, 11.3.

FT-IR (film): 3465, 2934, 2354, 1708, 1369, 1047, 889, 721 cm^{-1}.

HRMS (ESI-MS) *m/z* [M+H]$^+$ calcd for $C_{25}H_{27}N_2O_4$: 419.1965, found: 419.1975.
$[\alpha]^{22}_D$ = –5.8 (*c* 1.0, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



2-(8-(Benzyloxy)octan-3-yl)isoindoline-1,3-dione (21). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-6**. The product was purified by column chromatography on silica gel (1:12 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 219 mg, 99% yield, 89% ee; (*R*,*R*)-**L1**: 222 mg, 99% yield, 90% ee.

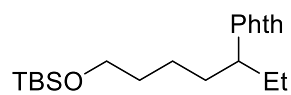
SFC analysis: The ee was determined via SFC on a CHIRALPAK IE-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 6.6 min (minor), 7.0 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.74 – 7.67 (m, 2H), 7.35 – 7.28 (m, 4H), 7.28 – 7.23 (m, 1H), 4.46 (s, 2H), 4.17 – 4.04 (m, 1H), 3.41 (t, *J* = 6.5 Hz, 2H), 2.15 – 1.98 (m, 2H), 1.83 – 1.66 (m, 2H), 1.61 – 1.51 (m, 2H), 1.46 – 1.17 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 138.8, 134.0, 132.0, 128.5, 127.7, 127.6, 123.2, 73.0, 70.4, 54.0, 32.3, 29.7, 26.7, 26.0, 25.7, 11.3.

FT-IR (film): 3462, 2922, 2354, 1708, 1367, 1066, 890, 721 cm^{-1}.

HRMS (ESI-MS) *m/z* [M+H]$^+$ calcd for $C_{23}H_{28}NO_3$: 366.2064, found: 366.2064.
$[\alpha]^{22}_D$ = –5.2 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L1**.



2-(7-((*tert*-Butyldimethylsilyl)oxy)heptan-3-yl)isoindoline-1,3-dione (22). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-7**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 222 mg, 99% yield, 89% ee; (*R*,*R*)-**L1**: 225 mg, 99% yield, 89% ee.

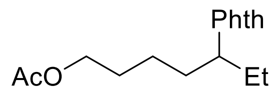
SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (2% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 5.1 min (minor), 5.4 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.73 – 7.67 (m, 2H), 4.20 – 4.03 (m, 1H), 3.54 (t, *J* = 6.4 Hz, 2H), 2.15 – 1.98 (m, 2H), 1.83 – 1.67 (m, 2H), 1.58 – 1.40 (m, 2H), 1.35 – 1.22 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H), 0.81 (s, 9H), –0.02 (d, *J* = 2.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 133.9, 132.0, 123.2, 63.0, 54.0, 32.5, 32.1, 26.0, 25.7, 23.1, 18.4, 11.3, –5.20, –5.22.

FT-IR (film): 3468, 2354, 1714, 1470, 1250, 1101, 840, 721 cm^{-1}.

HRMS (ESI-MS) *m/z* [M+H]$^+$ calcd for $C_{21}H_{34}NO_3Si$: 376.2302, found: 376.2305.
$[\alpha]^{22}_D$ = –4.8 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L1**.



5-(1,3-Dioxoisoindolin-2-yl)heptyl acetate (23). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-8**. The product was purified by column chromatography on silica gel (1:2 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 140 mg, 77% yield, 90% ee; (*R*,*R*)-**L1**: 145 mg, 80% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IF-3 column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 3.7 min (minor), 4.1 min (major).

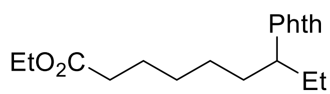
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.73 – 7.68 (m, 2H), 4.17 – 4.07 (m, 1H), 4.05 – 3.93 (m, 2H), 2.18 – 2.00 (m, 2H), 1.98 (s, 3H), 1.82 – 1.54 (m, 4H), 1.40 – 1.22 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 169.0, 134.0, 131.9, 123.3, 64.3, 53.8, 31.9, 28.3, 25.7, 23.2, 21.1, 11.3.

FT-IR (film): 3460, 2354, 1714, 1367, 1232, 1050, 860, 721 cm^{-1}.

HRMS (ESI-MS) *m/z* [M+H]$^+$ calcd for $C_{17}H_{22}NO_4$: 304.1543, found: 304.1549.

$[\alpha]^{22}_D$ = –9.7 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



Ethyl 7-(1,3-dioxoisoindolin-2-yl)nonanoate (24). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-9**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 186 mg, 94% yield, 89% ee; (*R*,*R*)-**L1**: 193 mg, 97% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IF-3 column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 5.9 min (minor), 6.5 min (major).

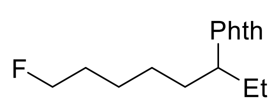
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.75 – 7.65 (m, 2H), 4.19 – 4.07 (m, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.23 (t, *J* = 7.2 Hz, 2H), 2.15 – 1.96 (m, 2H), 1.83 – 1.66 (m, 2H), 1.65 – 1.48 (m, 2H), 1.44 – 1.15 (m, 4H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 169.0, 134.0, 131.9, 123.2, 60.3, 53.9, 34.4, 32.2, 28.9, 26.5, 25.7, 24.9, 14.4, 11.2.

FT-IR (film): 3462, 2925, 2354, 1714, 1367, 1192, 1058, 861, 721 cm^{-1}.

HRMS (ESI-MS) *m/z* [M+H]$^+$ calcd for $C_{19}H_{26}NO_4$: 332.1856, found: 332.1867.

$[\alpha]^{22}_D$ = –7.3 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L1**.



2-(8-Fluorooctan-3-yl)isoindoline-1,3-dione (25). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-10**. The product was purified by column chromatography on silica gel (1:12 EtOAc/hexanes). Colorless oil.

(S,S)-**L1**: 158 mg, 95% yield, 90% ee; (R,R)-**L1**: 154 mg, 93% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IF-3 column (3% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (S,S)-**L1**: 3.7 min (minor), 4.1 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.75 – 7.67 (m, 2H), 4.44 (t, J = 6.1 Hz, 1H), 4.32 (t, J = 6.1 Hz, 1H), 4.17 – 4.06 (m, 1H), 2.17 – 1.99 (m, 2H), 1.82 – 1.55 (m, 4H), 1.50 – 1.18 (m, 4H), 0.86 (t, J = 7.4 Hz, 3H).

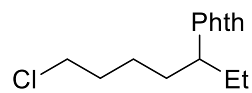
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 134.0, 131.9, 123.3, 84.1 (d, J = 165 Hz), 53.9, 32.2, 30.3 (d, J = 19.2 Hz), 26.4, 25.7, 25.0 (d, J = 5.1 Hz), 11.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ –218.2.

FT-IR (film): 3463, 2352, 1708, 1367, 1049, 892, 720 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{16}H_{21}FNO_2$: 278.1551, found: 278.1554.

$[\alpha]^{22}_D$ = –4.2 (c 1.0, $CHCl_3$); 90% ee, from (S,S)-**L1**.



2-(7-Chloroheptan-3-yl)isoindoline-1,3-dione (26). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-11**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). Colorless oil.

(S,S)-**L1**: 144 mg, 86% yield, 91% ee; (R,R)-**L1**: 153 mg, 91% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK AD-3 column (2% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (S,S)-**L1**: 9.2 min (minor), 10.1 min (major).

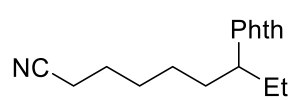
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.75 – 7.67 (m, 2H), 4.18 – 4.06 (m, 1H), 3.47 (t, J = 6.6 Hz, 2H), 2.19 – 1.98 (m, 2H), 1.85 – 1.67 (m, 4H), 1.49 – 1.31 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 134.0, 131.9, 123.3, 53.7, 44.9, 32.3, 31.6, 25.7, 24.1, 11.3.

FT-IR (film): 3461, 2928, 2353, 1710, 1369, 1168, 1054, 790, 720 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{15}H_{19}ClNO_2$: 280.1099, found: 280.1099.

$[\alpha]^{22}_D$ = –9.4 (c 1.0, $CHCl_3$); 91% ee, from (S,S)-**L1**.



7-(1,3-Dioxoisoindolin-2-yl)nonanenitrile (27). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-12**. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes). Colorless oil.

(S,S)-**L1**: 157 mg, 92% yield, 90% ee; (R,R)-**L1**: 160 mg, 94% yield, 89% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IF-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (S,S)-**L1**: 3.6 min (minor), 3.8 min (major).

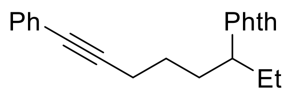
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.75 – 7.68 (m, 2H), 4.16 – 4.05 (m, 1H), 2.29 (t, *J* = 7.1 Hz, 2H), 2.18 – 1.99 (m, 2H), 1.84 – 1.65 (m, 2H), 1.65 – 1.56 (m, 2H), 1.56 – 1.17 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 134.1, 131.9, 123.3, 119.8, 53.8, 32.0, 28.4, 26.0, 25.7, 25.4, 17.2, 11.2.

FT-IR (film): 3460, 2918, 2246, 1705, 1366, 1056, 864, 728 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{17}H_{21}N_2O_2$: 285.1598, found: 285.1605.

$[\alpha]^{22}_D$ = –4.5 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



2-(8-Phenyloct-7-yn-3-yl)isoindoline-1,3-dione (28). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-13**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 151 mg, 76% yield, 91% ee; (*R*,*R*)-**L1**: 159 mg, 80% yield, 91% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 6.7 min (major), 7.4 min (minor).

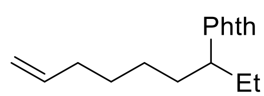
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2H), 7.76 – 7.68 (m, 2H), 7.43 – 7.34 (m, 2H), 7.32 – 7.23 (m, 3H), 4.25 – 4.13 (m, 1H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.34 – 2.21 (m, 1H), 2.19 – 2.03 (m, 1H), 2.00 – 1.89 (m, 1H), 1.89 – 1.76 (m, 1H), 1.63 – 1.51 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 134.0, 131.9, 131.7, 128.3, 127.7, 124.0, 123.3, 89.7, 81.2, 53.5, 31.5, 26.0, 25.8, 19.2, 11.3.

FT-IR (film): 3461, 2928, 2234, 1709, 1366, 1048, 797, 726 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{22}H_{22}NO_2$: 332.1645, found: 332.1644.

$[\alpha]^{22}_D$ = –10.7(*c* 1.0, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



2-(Non-8-en-3-yl)isoindoline-1,3-dione (29). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-14**. The product was purified by column chromatography on silica gel (1:5 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 101 mg, 62% yield, 89% ee; (*R*,*R*)-**L1**: 98 mg, 60% yield, 89% ee.

SFC Analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (2% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 7.3 min (minor), 8.2 min (major).

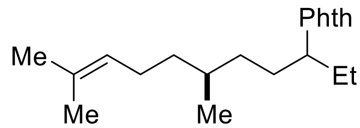
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.74 – 7.68 (m, 2H), 5.84 – 5.66 (m, 1H), 5.05 – 4.77 (m, 2H), 4.18 – 4.04 (m, 1H), 2.15 – 1.94 (m, 4H), 1.84 – 1.66 (m, 2H), 1.49 – 1.16 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 138.9, 134.0, 132.0, 123.2, 114.5, 54.0, 33.7, 32.2, 28.7, 26.3, 25.7, 11.3.

FT-IR (film): 3466, 2926, 2359, 1710, 1358, 1048, 911, 723 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{17}H_{22}NO_2$: 272.1645, found: 272.1632.

$[\alpha]^{22}_D$ = –8.7 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L1**.



2-((6*S*)-6,10-Dimethylundec-9-en-3-yl)isoindoline-1,3-dione (30, 31). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-15**. The product was purified by column chromatography on silica gel (1:12 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 150 mg, 77% yield, 96:4 d.r.; (*R*,*R*)-**L1**: 153 mg, 78% yield, 4:96 d.r.

SFC analysis: The d.r. was determined via SFC on a CHIRALPAK IF-3 column (2% CH_3CN in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 9.1 min (minor), 11.9 min (major).

NMR data for the product from (*S*,*S*)-**L1**:

^1H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.74 – 7.67 (m, 2H), 5.08 – 4.99 (m, 1H), 4.12 – 4.01 (m, 1H), 2.14 – 1.71 (m, 6H), 1.64 (s, 3H), 1.54 (s, 3H), 1.46 – 1.01 (m, 5H), 0.86 (t, *J* = 7.6 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 133.9, 132.0, 131.2, 125.0, 123.2, 54.6, 36.9, 34.1, 32.4, 29.9, 25.8, 25.7, 25.6, 19.7, 17.7, 11.3.

NMR data for the product from (*R*,*R*)-**L1**:

^1H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.74 – 7.67 (m, 2H), 5.08 – 5.00 (m, 1H), 4.14 – 4.02 (m, 1H), 2.17 – 1.99 (m, 2H), 1.98 – 1.67 (m, 4H), 1.65 (s, 3H), 1.54 (s, 3H), 1.46 – 1.17 (m, 3H), 1.16 – 0.95 (m, 2H), 0.86 (t, *J* = 7.6 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H).

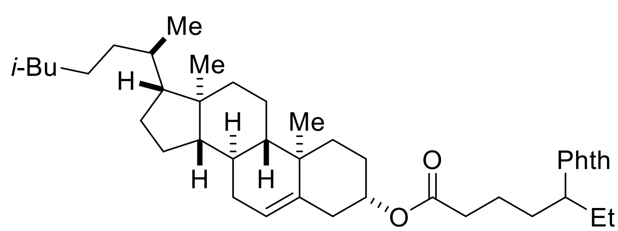
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 133.9, 132.0, 131.2, 125.0, 123.2, 54.4, 37.1, 33.9, 32.2, 29.7, 25.83, 25.81, 25.6, 19.6, 17.7, 11.3.

FT-IR (film): 3465, 2922, 1709, 1455, 1368, 1062, 884, 718 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{21}H_{30}NO_2$: 328.2271, found: 328.2273.

$[\alpha]^{22}_D$ = +0.8 (*c* 1.0, $CHCl_3$); 96:4 d.r., from (*S*,*S*)-**L1**.

$[\alpha]^{22}_D$ = +15.3 (*c* 1.0, $CHCl_3$); 4:96 d.r., from (*R*,*R*)-**L1**.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 5-(1,3-dioxoisoindolin-2-yl)heptanoate (32, 33). The title compound was synthesized according to

GP-5 from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-16**. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 336 mg, 87% yield, 92:8 d.r.; (*R*,*R*)-**L1**: 324 mg, 84% yield, 8:92 d.r.

SFC analysis: The d.r. was determined via SFC on a CHIRALPAK IG-3 column (25% MeOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 10.7 min (minor), 11.7 min (major).

NMR data for the product from (*S*,*S*)-**L1**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.75 – 7.66 (m, 2H), 5.39 – 5.31 (m, 1H), 4.63 – 4.51 (m, 1H), 4.19 – 4.06 (m, 1H), 2.35 – 2.20 (m, 4H), 2.19 – 1.90 (m, 4H), 1.88 – 1.69 (m, 5H), 1.64 – 1.40 (m, 9H), 1.40 – 1.21 (m, 4H), 1.21 – 1.04 (m, 7H), 1.03 – 0.89 (m, 9H), 0.88 – 0.81 (m, 9H), 0.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 168.9, 139.8, 134.0, 131.9, 123.3, 122.7, 74.0, 56.8, 56.3, 53.6, 50.1, 42.4, 39.9, 39.6, 38.2, 37.1, 36.7, 36.3, 35.9, 34.3, 32.02, 31.98, 31.7, 28.4, 28.1, 27.9, 25.7, 24.4, 24.0, 23.0, 22.7, 22.3, 21.2, 19.4, 18.8, 12.0, 11.2.

NMR data for the product from (*R*,*R*)-**L1**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.74 – 7.67 (m, 2H), 5.38 – 5.29 (m, 1H), 4.62 – 4.50 (m, 1H), 4.18 – 4.07 (m, 1H), 2.35 – 2.20 (m, 4H), 2.20 – 1.90 (m, 4H), 1.90 – 1.67 (m, 5H), 1.65 – 1.40 (m, 9H), 1.40 – 1.22 (m, 4H), 1.22 – 1.02 (m, 7H), 1.03 – 0.88 (m, 9H), 0.88 – 0.81 (m, 9H), 0.66 (s, 3H).

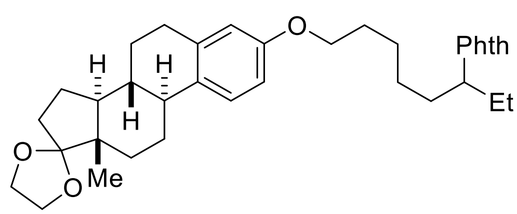
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 168.9, 139.8, 134.0, 131.9, 123.3, 122.7, 74.0, 56.8, 56.3, 53.6, 50.1, 42.4, 39.9, 39.6, 38.2, 37.1, 36.7, 36.3, 35.9, 34.2, 32.02, 31.97, 31.7, 28.4, 28.1, 27.9, 25.7, 24.4, 24.0, 23.0, 22.7, 22.3, 21.2, 19.4, 18.8, 12.0, 11.2.

FT-IR (film): 3460, 2353, 1714, 1361, 1168, 1020, 892, 721 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{42}H_{65}N_2O_4$: 661.4939, found: 661.4949.

$[\alpha]^{22}_D$ = –26.4 (*c* 1.0, $CHCl_3$); 92:8 d.r., from (*S*,*S*)-**L1**.

$[\alpha]^{22}_D$ = –17.8 (*c* 1.0, $CHCl_3$); 8:92 d.r., from (*R*,*R*)-**L1**.



2-(8-(((8*R*,9*S*,13*S*,14*S*)-13-Methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)octan-3-yl)isoindoline-1,3-dione (34, 35). The title compound was synthesized according to **GP-5** from 2-(1-chloropropyl)isoindoline-1,3-dione and **Zn-17**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L1**: 307 mg, 90% yield, 94:6 d.r.; (*R*,*R*)-**L1**: 300 mg, 88% yield, 6:94 d.r.

SFC analysis: The d.r. was determined via SFC on a CHIRALCEL OJ-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 7.0 min (major), 7.5 min (minor).

NMR data for the product from (*S*,*S*)-**L1**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.74 – 7.65 (m, 2H), 7.16 (d, *J* = 8.7 Hz, 1H), 6.65 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 4.17 – 4.07 (m, 1H), 3.99 – 3.83 (m, 6H), 2.90 – 2.74 (m, 2H), 2.37 – 2.17 (m, 2H), 2.17 – 1.97 (m, 3H), 1.92 – 1.58 (m, 9H), 1.56 – 1.23 (m, 9H), 0.874 (s, 3H), 0.865 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 157.0, 138.1, 134.0, 132.7, 132.0, 126.4, 123.2, 119.6, 114.6, 112.2, 67.8, 65.4, 64.7, 54.0, 49.5, 46.3, 43.8, 39.2, 34.4, 32.3, 30.9, 29.9, 29.3, 27.2, 26.6, 26.3, 25.9, 25.7, 22.5, 14.5, 11.3.

NMR data for the product from (*R*,*R*)-**L1**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.75 – 7.66 (m, 2H), 7.16 (d, *J* = 8.7 Hz, 1H), 6.65 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.58 (d, *J* = 2.7 Hz, 1H), 4.19 – 4.06 (m, 1H), 4.02 – 3.80 (m, 6H), 2.91 – 2.73 (m, 2H), 2.37 – 2.17 (m, 2H), 2.17 – 1.96 (m, 3H), 1.95 – 1.57 (m, 9H), 1.57 – 1.24 (m, 9H), 0.88 (s, 3H), 0.87 (t, *J* = 7.6 Hz, 3H).

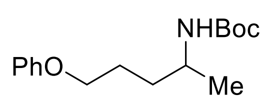
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 157.0, 138.0, 134.0, 132.6, 132.0, 126.4, 123.2, 119.6, 114.6, 112.1, 67.8, 65.4, 64.7, 54.0, 49.5, 46.3, 43.8, 39.2, 34.4, 32.3, 30.9, 29.9, 29.3, 27.1, 26.6, 26.3, 25.9, 25.7, 22.5, 14.5, 11.3.

FT-IR (film): 3460, 2918, 2352, 1709, 1605, 1470, 1366, 1246, 1050, 724 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{36}H_{46}NO_5$: 572.3371, found: 572.3368.

$[\alpha]^{22}_{D}$ = +9.5 (*c* 1.0, $CHCl_3$); 94:6 d.r., from (*S*,*S*)-**L1**.

$[\alpha]^{22}_{D}$ = +20.4 (*c* 1.0, $CHCl_3$); 6:94 d.r., from (*R*,*R*)-**L1**.



***tert*-Butyl (5-phenoxypentan-2-yl)carbamate (36).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)alaninate and **Zn-18**. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 109 mg, 65% yield, 90% ee; (*R*,*R*)-**L2**: 114 mg, 68% yield, 90% ee.

After recrystallization using *n*-pentane/hexanes: (*S*,*S*)-**L2**: 92 mg, 90% ee → 66 mg, 72% yield (47% yield overall), >99% ee; (*R*,*R*)-**L2**: 86 mg, 90% ee → 65 mg, 76% yield (51% yield overall), >99% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OJ column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 12.3 min (minor), 17.8 min (major).

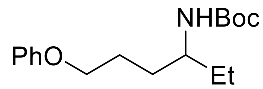
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 2H), 6.97 – 6.87 (m, 3H), 4.41 (d, *J* = 8.6 Hz, 1H), 3.96 (td, *J* = 6.3, 1.2 Hz, 2H), 3.70 (q, *J* = 7.7, 7.2 Hz, 1H), 1.89 – 1.77 (m, 2H), 1.68 – 1.51 (m, 2H), 1.45 (s, 9H), 1.16 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 155.5, 129.5, 120.7, 114.6, 79.1, 67.6, 46.4, 34.0, 28.6, 26.1, 21.6.

FT-IR (film): 3372, 2967, 1690, 1499, 1247, 1173, 751 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{16}H_{26}NO_3$: 280.1907, found: 280.1912.

$[\alpha]^{23}_D$ = –6.2 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (6-phenoxyhexan-3-yl)carbamate (37).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)butanoate and **Zn-18**. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 137 mg, 79% yield, 90% ee; (*R*,*R*)-**L2**: 143 mg, 81% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 8.4 min (major), 9.1 min (minor).

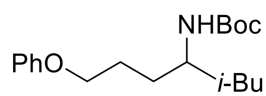
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 6.97 – 6.85 (m, 3H), 4.36 – 4.30 (m, 1H), 3.97 (t, *J* = 6.3 Hz, 2H), 3.62 – 3.48 (m, 1H), 1.93 – 1.77 (m, 2H), 1.73 – 1.52 (m, 2H), 1.47 – 1.42 (m, 11H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 156.0, 129.5, 120.7, 114.6, 79.1, 67.7, 51.9, 31.8, 28.6, 26.0, 10.4.

FT-IR (film): 3345, 2966, 1698, 1498, 1246, 1174, 1091, 754, 692 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{17}H_{28}NO_3$: 294.2064, found: 294.2061.

$[\alpha]^{23}_D$ = –9.9 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (6-methyl-1-phenoxyheptan-4-yl)carbamate (38).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)leucinate and **Zn-18**. The product was purified by column chromatography on silica gel (15:85 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 139 mg, 72% yield, 90% ee; (*R*,*R*)-**L2**: 134 mg, 70% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK AD column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 5.2 min (minor), 6.6 min (major).

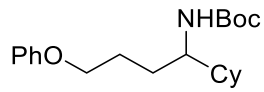
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 2H), 6.97 – 6.86 (m, 3H), 4.26 (d, *J* = 9.4 Hz, 1H), 3.97 (t, *J* = 6.3 Hz, 2H), 3.76 – 3.63 (m, 1H), 1.92 – 1.74 (m, 2H), 1.74 – 1.60 (m, 2H), 1.45 – 1.42 (m, 10H), 1.35 – 1.22 (m, 2H), 0.91 (dd, *J* = 6.6, 4.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 155.8, 129.5, 120.7, 114.6, 79.0, 67.8, 48.7, 45.3, 32.8, 28.6, 25.9, 25.1, 23.3, 22.4.

FT-IR (film): 3346, 2918, 1691, 1497, 1246, 1173, 1037, 755, 692 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{19}H_{32}NO_3$: 322.2377, found: 322.2378.

$[\alpha]^{23}_D$ = –14.8 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (1-cyclohexyl-4-phenoxybutyl)carbamate (39).** The title compound was synthesized according to **GP-7** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetate and **Zn-18**. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 138 mg, 66% yield, 88% ee; (*R*,*R*)-**L2**: 142 mg, 68% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 8.0 min (major), 14.2 min (minor).

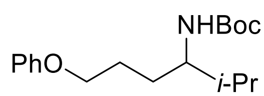
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 6.73 (m, 5H), 4.52 – 4.28 (m, 1H), 3.97 (t, *J* = 6.1 Hz, 2H), 3.57 – 3.33 (m, 1H), 1.99 – 1.58 (m, 9H), 1.49 – 1.38 (m, 10H), 1.38 – 0.84 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 156.1, 155.8, 150.6, 129.6, 129.5, 126.2, 121.6, 120.7, 114.6, 80.1, 79.0, 67.7, 66.0, 58.6, 55.0, 42.6, 41.3, 29.8, 29.7, 29.2, 28.6, 28.5, 28.4, 26.6, 26.44, 26.42, 26.3, 26.2, 26.1.

FT-IR (film): 3348, 2927, 2853, 1704, 1496, 1246, 1166, 753, 691 cm^{-1}.

HRMS (ESI-MS) *m/z* [M+H]$^+$ calcd for $C_{21}H_{34}NO_3$: 348.2533, found: 348.2539.

$[\alpha]^{23}_D$ = –5.3 (*c* 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (2-methyl-6-phenoxyhexan-3-yl)carbamate (40).** The title compound was synthesized according to **GP-7** from 1,3-dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)valinate and **Zn-18**. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 122 mg, 66% yield, 89% ee; (*R*,*R*)-**L2**: 115 mg, 62% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 7.7 min (minor), 13.0 min (major).

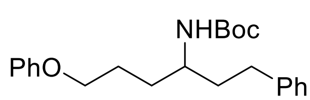
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 6.83 (m, 5H), 4.55 – 4.25 (m, 1H), 3.97 (t, *J* = 6.2 Hz, 2H), 3.55 – 3.39 (m, 1H), 1.98 – 1.34 (m, 14H), 1.19 – 0.82 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 156.2, 155.8, 150.5, 129.6, 129.5, 126.2, 121.5, 120.7, 114.6, 80.1, 79.0, 67.7, 58.8, 55.4, 32.5, 31.5, 29.3, 28.6, 28.4, 26.3, 19.2, 17.8.

FT-IR (film): 3356, 2963, 1703, 1498, 1246, 1174, 754, 691 cm^{-1}.

HRMS (ESI-MS) *m/z* [M+H]$^+$ calcd for $C_{18}H_{30}NO_3$: 308.2222, found: 308.2216.

$[\alpha]^{23}_D$ = +0.4 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (6-phenoxy-1-phenylhexan-3-yl)carbamate (41).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-

phenylbutanoate and **Zn-18**. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 176 mg, 79% yield, 90% ee; (*R*,*R*)-**L2**: 181 mg, 82% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 9.1 min (minor), 12.1 min (major).

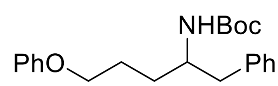
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 4H), 7.22 – 7.15 (m, 3H), 6.98 – 6.88 (m, 3H), 4.38 (d, *J* = 9.4 Hz, 1H), 3.97 (t, *J* = 6.2 Hz, 2H), 3.75 – 3.65 (m, 1H), 2.77 – 2.59 (m, 2H), 1.93 – 1.50 (m, 6H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 155.9, 142.1, 129.6, 128.54, 128.50, 126.0, 120.7, 114.6, 79.2, 67.6, 50.5, 37.9, 32.5, 32.4, 28.6, 25.9.

FT-IR (film): 3344, 2932, 1704, 1496, 1246, 1168, 1037, 753, 699 cm^{-1}.

HRMS (ESI-MS) *m/z* [M+H]$^+$ calcd for $C_{23}H_{32}NO_3$: 370.2377, found: 370.2377.

$[\alpha]^{23}_D$ = +3.9 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (5-phenoxy-1-phenylpentan-2-yl)carbamate (42).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)phenylalaninate and **Zn-18**. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 162 mg, 76% yield, 90% ee; (*R*,*R*)-**L2**: 164 mg, 77% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 13.1 min (minor), 14.0 min (major).

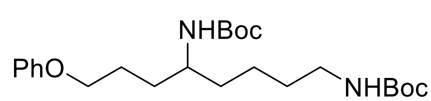
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.17 (m, 7H), 6.98 – 6.90 (m, 1H), 6.89 – 6.84 (m, 2H), 4.41 (d, *J* = 9.1 Hz, 1H), 3.94 (t, *J* = 6.2 Hz, 2H), 3.88 (s, 1H), 2.88 – 2.73 (m, 2H), 1.95 – 1.64 (m, 4H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 155.6, 138.2, 129.7, 129.5, 128.5, 126.5, 120.7, 114.6, 79.2, 67.5, 51.5, 41.7, 30.9, 28.5, 26.1.

FT-IR (film): 3346, 2932, 1698, 1496, 1365, 1246, 1168, 754, 693 cm^{-1}.

HRMS (ESI-MS) *m/z* [M+H]$^+$ calcd for $C_{22}H_{30}NO_3$: 356.2220, found: 356.2221.

$[\alpha]^{23}_D$ = +13.2 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



Di-*tert*-butyl (8-phenoxyoctane-1,5-diyl)dicarbamate (43). The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl N^2,N^6-bis(*tert*-butoxycarbonyl)lysinate and **Zn-18**. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes) and was then extracted in hexanes to separate it from phthalimide. White solid.

(S,S)-**L2**: 165 mg, 63% yield, 91% ee; (R,R)-**L2**: 159 mg, 61% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (7% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (S,S)-**L2**: 10.1 min (minor), 12.2 min (major).

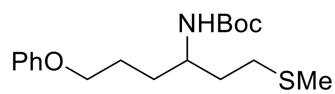
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2H), 6.97 – 6.86 (m, 3H), 4.59 (s, 1H), 4.36 (d, J = 9.3 Hz, 1H), 3.95 (t, J = 6.2 Hz, 2H), 3.65 – 3.53 (m, 1H), 3.15 – 3.05 (m, 2H), 1.87 – 1.60 (m, 4H), 1.54 – 1.37 (m, 24H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 156.2, 156.0, 129.5, 120.7, 114.6, 79.1, 67.6, 50.3, 40.5, 35.7, 32.3, 31.7, 29.9, 28.6, 26.0, 23.2, 22.8, 14.3.

FT-IR (film): 3348, 2933, 1697, 1521, 1365, 1247, 1169, 752 cm^{-1}.

LC-MS (ESI-MS) m/z $[M+Na]^+$ calcd for $C_{24}H_{40}N_2NaO_5$: 459.3, found: 459.3.

$[\alpha]^{23}_D$ = –6.9 (c 1.0, $CHCl_3$); 91% ee, from (S,S)-**L2**.



***tert*-Butyl (1-(methylthio)-6-phenoxyhexan-3-yl)carbamate (44).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)methioninate and **Zn-18**. The product was purified by column chromatography on silica gel (3:7 EtOAc/hexanes). White solid.

(S,S)-**L2**: 130 mg, 64% yield, 91% ee; (R,R)-**L2**: 132 mg, 65% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (7% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (S,S)-**L2**: 11.0 min (minor), 11.7 min (major).

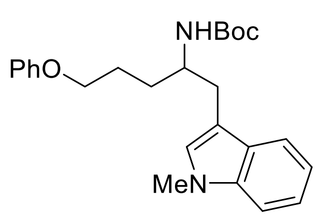
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 2H), 6.98 – 6.85 (m, 3H), 4.40 (d, J = 9.3 Hz, 1H), 3.97 (t, J = 6.1 Hz, 2H), 3.78 – 3.61 (m, 1H), 2.58 – 2.48 (m, 2H), 2.10 (s, 3H), 1.95 – 1.50 (m, 6H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 155.8, 129.6, 120.8, 114.6, 79.3, 67.5, 50.1, 35.6, 32.2, 30.9, 28.6, 26.0, 15.8.

FT-IR (film): 3346, 2918, 1694, 1498, 1246, 1173, 1038, 755, 692 cm^{-1}.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{18}H_{30}NO_3S$: 340.1941, found: 340.1949.

$[\alpha]^{23}_D$ = –2.1 (c 1.0, $CHCl_3$); 91% ee, from (S,S)-**L2**.



***tert*-Butyl (1-(1-methyl-1*H*-indol-3-yl)-5-phenoxypentan-2-yl)carbamate (45).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl N^{α}-(*tert*-butoxycarbonyl)-1-methyltryptophanate and **Zn-18**. The product was purified by column chromatography on silica gel (35:65 EtOAc/hexanes). White solid.

(S,S)-**L2**: 129 mg, 53% yield, 91% ee; (R,R)-**L2**: 145 mg, 59% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (7% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (S,S)-**L2**: 11.6 min (minor), 17.5 min (major).

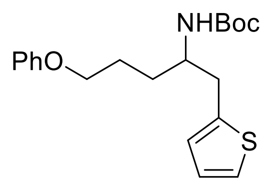
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 1H), 7.31 – 7.17 (m, 4H), 7.15 – 7.07 (m, 1H), 6.97 – 6.89 (m, 1H), 6.90 – 6.83 (m, 3H), 4.48 (d, J = 9.2 Hz, 1H), 4.02 – 3.92 (m, 3H), 3.75 (s, 3H), 2.96 (d, J = 5.9 Hz, 2H), 1.96 – 1.69 (m, 4H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 155.8, 137.0, 129.5, 128.6, 127.6, 121.6, 120.7, 119.4, 119.0, 114.6, 110.6, 109.2, 79.1, 67.6, 50.9, 32.8, 31.1, 30.9, 28.6, 26.2.

FT-IR (film): 3382, 2934, 1710, 1496, 1247, 1173, 1053, 742 cm^{-1}.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{25}H_{33}N_2O_3$: 409.2486, found: 409.2481.

$[\alpha]^{23}_{D}$ = +6.9 (c 1.0, $CHCl_3$); 91% ee, from (S,S)-**L2**.



***tert*-Butyl (5-phenoxy-1-(thiophen-2-yl)pentan-2-yl)carbamate (46).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-3-(thiophen-2-yl)propanoate and **Zn-18**. The product was purified by column chromatography on silica gel (15:85 EtOAc/hexanes). White solid.

(S,S)-**L2**: 149 mg, 69% yield, 92% ee; (R,R)-**L2**: 155 mg, 72% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (S,S)-**L2**: 13.9 min (minor), 19.2 min (major).

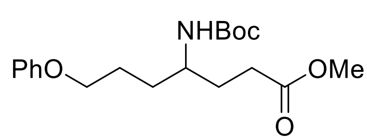
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.19 – 7.13 (m, 1H), 6.96 – 6.91 (m, 2H), 6.90 – 6.86 (m, 2H), 6.84 – 6.81 (m, 1H), 4.54 – 4.47 (m, 1H), 3.96 (t, J = 6.2 Hz, 2H), 3.90 – 3.81 (m, 1H), 3.13 – 2.96 (m, 2H), 1.91 – 1.80 (m, 2H), 1.77 – 1.49 (m, 2H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 155.6, 139.9, 129.6, 127.0, 126.3, 124.2, 120.8, 114.6, 79.4, 67.4, 51.2, 35.2, 30.7, 28.6, 26.1.

FT-IR (film): 3338, 2934, 1692, 1498, 1244, 1171, 753, 690 cm^{-1}.

LC-MS (ESI-MS) m/z $[M+Na]^+$ calcd for $C_{20}H_{27}NNaO_3S$: 384.2, found: 384.1.

$[\alpha]^{23}_{D}$ = +17.2 (c 1.0, $CHCl_3$); 92% ee, from (S,S)-**L2**.



Methyl 4-((*tert*-butoxycarbonyl)amino)-7-phenoxyheptanoate (47). The title compound was synthesized according to **GP-6** from 1-(1,3-dioxoisoindolin-2-yl) 5-methyl (*tert*-butoxycarbonyl)glutamate and **Zn-18**. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes) and was then extracted in hexanes to separate it from phthalimide. White solid.

(*S*,*S*)-**L2**: 145 mg, 69% yield, 93% ee; (*R*,*R*)-**L2**: 138 mg, 65% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OJ column (7% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 16.6 min (minor), 18.6 min (major).

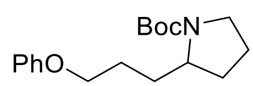
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 6.95 – 6.86 (m, 3H), 4.34 (d, *J* = 9.5 Hz, 1H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.67 (s, 3H), 3.65 – 3.61 (m, 1H), 2.40 (t, *J* = 7.5 Hz, 2H), 1.92 – 1.59 (m, 6H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 158.9, 155.7, 129.4, 120.6, 114.5, 79.2, 67.4, 51.7, 50.2, 32.4, 30.8, 30.7, 28.4, 25.8.

FT-IR (film): 3367, 2950, 1709, 1498, 1365, 1246, 1173, 756 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{29}NNaO_5$: 374.2, found: 374.2.

$[\alpha]^{23}_{D}$ = +0.9 (*c* 1.0, $CHCl_3$); 93% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl 2-(3-phenoxypropyl)pyrrolidine-1-carboxylate (48).** The title compound was synthesized according to **GP-6** from 1-(*tert*-butyl) 2-(1,3-dioxoisoindolin-2-yl) pyrrolidine-1,2-dicarboxylate and **Zn-18**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 119 mg, 65% yield, 90% ee; (*R*,*R*)-**L2**: 114 mg, 62% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 8.1 min (minor), 9.0 min (major).

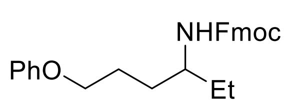
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 2H), 6.96 – 6.84 (m, 3H), 4.01 – 3.89 (m, 2H), 3.87 – 3.76 (m, 1H), 3.49 – 3.28 (m, 2H), 1.98 – 1.63 (m, 8H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 154.8, 129.5, 120.6, 114.6, 79.2, 67.7, 57.2, 46.7, 30.9, 28.7, 26.3, 23.9, 23.2.

FT-IR (film): 2970, 2873, 1694, 1393, 1246, 1173, 1108, 754, 692 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{18}H_{28}NO_3$: 306.2064, found: 306.2070.

$[\alpha]^{23}_{D}$ = –39.7 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



(9*H*-Fluoren-9-yl)methyl (6-phenoxyhexan-3-yl)carbamate (49). The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)butanoate and **Zn-18**. The product was purified by column chromatography on silica gel (2:3 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 181 mg, 73% yield, 88% ee; (*R*,*R*)-**L2**: 182 mg, 73% yield, 86% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 8.7 min (major), 9.9 min (minor).

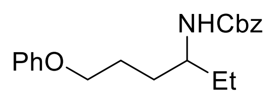
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.23 (m, 4H), 6.98 – 6.87 (m, 3H), 4.53 (d, *J* = 9.3 Hz, 1H), 4.45 (d, *J* = 6.7 Hz, 2H), 4.22 (t, *J* = 6.7 Hz, 1H), 3.97 (t, *J* = 6.1 Hz, 2H), 3.69 – 3.57 (m, 1H), 1.88 – 1.36 (m, 6H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 156.4, 144.2, 141.5, 129.6, 127.8, 127.2, 125.2, 120.8, 120.1, 114.6, 67.6, 66.4, 52.6, 47.6, 31.7, 28.5, 25.9, 10.3.

FT-IR (film): 3323, 2958, 1689, 1541, 1246, 1106, 737, 691 cm^{-1}.

LC-MS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{27}H_{30}NO_3$: 416.2, found: 416.2.

$[\alpha]^{23}_D$ = –8.2 (*c* 1.0, $CHCl_3$); 87% ee, from (*S*,*S*)-**L2**.



Benzyl (6-phenoxyhexan-3-yl)carbamate (50). The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-(((benzyloxy)carbonyl)amino)butanoate and **Zn-18**. The product was purified by column chromatography on silica gel (3:7 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 149 mg, 76% yield, 88% ee; (*R*,*R*)-**L2**: 155 mg, 79% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (7% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 10.8 min (minor), 12.1 min (major).

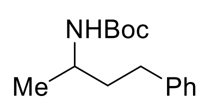
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 7H), 6.99 – 6.84 (m, 3H), 5.11 (s, 2H), 4.58 (d, *J* = 9.2 Hz, 1H), 3.97 (t, *J* = 6.2 Hz, 2H), 3.71 – 3.58 (m, 1H), 1.87 – 1.36 (m, 6H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 156.4, 136.8, 129.5, 128.6, 128.19, 128.17, 120.7, 114.6, 67.6, 66.7, 52.6, 31.6, 28.5, 25.9, 10.3.

FT-IR (film): 3325, 2961, 1694, 1498, 1244, 1093, 753, 693 cm^{-1}.

LC-MS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{26}NO_3$: 328.2, found: 328.2.

$[\alpha]^{23}_D$ = –3.4 (*c* 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (4-phenylbutan-2-yl)carbamate (51).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-19**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 108 mg, 72% yield, 81% ee; (*R*,*R*)-**L2**: 113 mg, 76% yield, 80% ee.

After recrystallization using *n*-pentane/hexanes: (*S*,*S*)-**L2**: 101 mg, 81% ee → 62 mg, 61% yield (44% yield overall), >99% ee; (*R*,*R*)-**L2**: 58 mg, 80% ee → 35 mg, 60% yield (46% yield overall), >99% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 8.9 min (minor), 11.0 min (major).

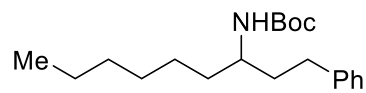
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 4.38 (s, 1H), 3.78 – 3.57 (m, 1H), 2.66 (td, *J* = 7.6, 3.9 Hz, 2H), 1.79 – 1.66 (m, 2H), 1.46 (s, 9H), 1.16 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 142.1, 128.50, 128.45, 125.9, 79.1, 46.5, 39.3, 32.6, 28.6, 21.5.

FT-IR (film): 3372, 2966, 1682, 1520, 1367, 1246, 1075, 744 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{15}H_{24}NO_2$: 250.1802, found: 250.1806.

$[\alpha]^{23}_D$ = +10.6 (*c* 1.0, $CHCl_3$); 81% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (1-phenylnonan-3-yl)carbamate (52).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-2**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 160 mg, 84% yield, 90% ee; (*R*,*R*)-**L2**: 159 mg, 83% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 5.9 min (minor), 7.9 min (major).

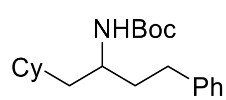
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 4.31 (d, *J* = 9.4 Hz, 1H), 3.66 – 3.57 (m, 1H), 2.76 – 2.56 (m, 2H), 1.83 – 1.56 (m, 2H), 1.48 – 1.44 (m, 10H), 1.40 – 1.25 (m, 9H), 0.92 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 142.3, 128.5, 125.9, 79.0, 50.7, 37.7, 35.8, 32.6, 31.9, 29.4, 28.6, 25.9, 22.7, 14.2.

FT-IR (film): 3347, 2930, 1694, 1519, 1366, 1246, 1173, 699 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{20}H_{34}NO_2$: 320.2584, found: 320.2586.

$[\alpha]^{23}_D$ = +16.0 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (1-cyclohexyl-4-phenylbutan-2-yl)carbamate (53).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-3**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 140 mg, 70% yield, 90% ee; (*R*,*R*)-**L2**: 146 mg, 73% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 5.8 min (minor), 7.6 min (major).

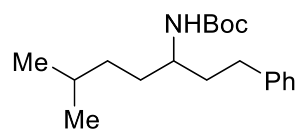
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 4.25 (d, *J* = 9.5 Hz, 1H), 3.80 – 3.68 (m, 1H), 2.75 – 2.56 (m, 2H), 1.89 – 1.56 (m, 7H), 1.46 (s, 9H), 1.39 – 1.06 (m, 6H), 1.01 – 0.77 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 142.4, 128.5, 128.5, 125.9, 79.0, 48.2, 43.9, 38.4, 34.6, 34.0, 33.1, 32.5, 28.6, 26.7, 26.5, 26.4.

FT-IR (film): 3346, 2921, 1698, 1522, 1365, 1247, 1166, 699 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{21}H_{34}NO_2$: 332.2584, found: 332.2581.

$[\alpha]^{23}_{D}$ = +8.8 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (6-methyl-1-phenylheptan-3-yl)carbamate (54).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-20**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 145 mg, 79% yield, 90% ee; (*R*,*R*)-**L2**: 143 mg, 78% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 5.4 min (minor), 6.6 min (major).

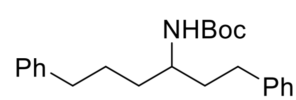
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.19 (d, *J* = 7.3 Hz, 3H), 4.31 (d, *J* = 9.4 Hz, 1H), 3.69 – 3.55 (m, 1H), 2.76 – 2.56 (m, 2H), 1.83 – 1.58 (m, 2H), 1.57 – 1.48 (m, 2H), 1.46 (s, 9H), 1.42 – 1.30 (m, 1H), 1.29 – 1.13 (m, 2H), 0.91 – 0.83 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 142.3, 128.5, 125.9, 79.1, 50.9, 37.7, 35.0, 33.6, 32.6, 28.6, 28.1, 22.8, 22.7.

FT-IR (film): 3328, 2950, 1681, 1537, 1366, 1176, 1026, 751, 699 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{19}H_{32}NO_2$: 306.2428, found: 306.2434.

$[\alpha]^{23}_{D}$ = +8.0 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (1,6-diphenylhexan-3-yl)carbamate (55).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-21**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 161 mg, 76% yield, 90% ee; (*R*,*R*)-**L2**: 162 mg, 76% yield, 89% ee.

After recrystallization using *n*-pentane/hexanes: (*S*,*S*)-**L2**: 150 mg, 90% ee → 125 mg, 83% yield (63% yield overall), 97% ee; (*R*,*R*)-**L2**: 105 mg, 89% ee → 83 mg, 79% yield (60% yield overall), 97% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (7% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 6.3 min (minor), 7.0 min (major).

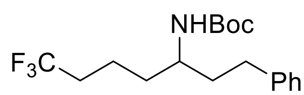
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 4H), 7.24 – 7.14 (m, 6H), 4.31 (d, *J* = 9.4 Hz, 1H), 3.75 – 3.63 (m, 1H), 2.73 – 2.56 (m, 4H), 1.84 – 1.60 (m, 4H), 1.58 – 1.38 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 142.4, 142.2, 128.53, 128.49, 128.47, 128.4, 125.93, 125.85, 79.1, 50.5, 37.7, 35.8, 35.3, 32.5, 28.6, 27.8.

FT-IR (film): 3340, 2934, 1694, 1496, 1365, 1246, 1172, 746, 699 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{23}H_{32}NO_2$: 354.2428, found: 354.2434.

$[\alpha]^{23}_D$ = +8.1 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl butyl (7,7,7-trifluoro-1-phenylheptan-3-yl)carbamate (56).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-22**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 159 mg, 77% yield, 90% ee; (*R*,*R*)-**L2**: 157 mg, 76% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 9.7 min (minor), 16.0 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 4.30 (d, *J* = 9.4 Hz, 1H), 3.76 – 3.55 (m, 1H), 2.77 – 2.57 (m, 2H), 2.22 – 1.95 (m, 2H), 1.86 – 1.73 (m, 1H), 1.71 – 1.52 (m, 4H), 1.49 – 1.40 (m, 10H).

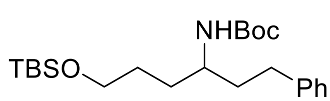
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 141.8, 128.6, 128.5, 127.2 (q, J = 276 Hz), 126.1, 79.4, 50.0, 37.7, 34.9, 33.6 (q, J = 28.4 Hz), 32.5, 28.5, 18.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ –66.3.

FT-IR (film): 3362, 2946, 1681, 1520, 1248, 1175, 746, 700 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{18}H_{27}F_3NO_2$: 346.1988, found: 346.1986.

$[\alpha]^{23}_D$ = +9.3 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (6-((*tert*-butyldimethylsilyl)oxy)-1-phenylhexan-3-yl)carbamate (57).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-23**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L2**: 210 mg, 86% yield, 89% ee; (*R*,*R*)-**L2**: 205 mg, 84% yield, 87% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OD column (5% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 4.9 min (major), 5.6 min (minor).

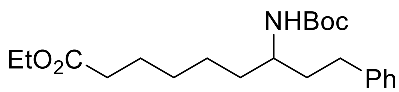
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 2H), 7.22 – 7.14 (m, 3H), 4.45 (d, *J* = 9.1 Hz, 1H), 3.68 – 3.58 (m, 3H), 2.75 – 2.57 (m, 2H), 1.86 – 1.63 (m, 2H), 1.60 – 1.39 (m, 13H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 142.2, 128.5, 125.9, 79.0, 63.0, 50.5, 37.8, 32.6, 31.9, 29.1, 28.6, 26.1, 18.5, -5.2.

FT-IR (film): 3348, 2929, 2857, 1702, 1365, 1252, 1174, 1101, 836, 776 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{23}H_{42}NO_3Si$: 408.2928, found: 408.2920.

$[\alpha]^{23}_D$ = +16.1 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



Ethyl 7-((*tert*-butoxycarbonyl)amino)-9-phenylnonanoate (58). The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-9**. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L2**: 175 mg, 77% yield, 90% ee; (*R*,*R*)-**L2**: 168 mg, 74% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OD column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 4.7 min (minor), 5.3 min (major).

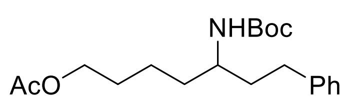
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 2H), 7.17 – 7.09 (m, 3H), 4.30 (d, *J* = 9.4 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.59 (s, 1H), 2.71 – 2.51 (m, 2H), 2.24 (t, *J* = 7.5 Hz, 2H), 1.78 – 1.51 (m, 4H), 1.47 – 1.24 (m, 15H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 155.8, 142.2, 128.5, 128.4, 125.9, 79.0, 60.3, 50.6, 37.7, 35.6, 34.3, 32.5, 29.1, 28.5, 25.6, 25.0, 14.4.

FT-IR (film): 3368, 2935, 1711, 1514, 1366, 1247, 1174, 699 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{22}H_{36}NO_4$: 378.2639, found: 378.2642.

$[\alpha]^{23}_D$ = +14.8 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



5-((*tert*-Butoxycarbonyl)amino)-7-phenylheptyl acetate (59). The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-8**. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 158 mg, 75% yield, 90% ee; (*R*,*R*)-**L2**: 162 mg, 77% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 12.0 min (minor), 17.7 min (major).

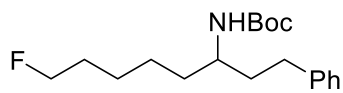
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.21 – 7.13 (m, 3H), 4.33 (d, *J* = 9.4 Hz, 1H), 4.04 (t, *J* = 6.6 Hz, 2H), 3.66 – 3.59 (m, 1H), 2.77 – 2.55 (m, 2H), 2.03 (s, 3H), 1.88 – 1.56 (m, 4H), 1.54 – 1.32 (m, 13H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 155.8, 142.1, 128.49, 128.45, 125.9, 79.1, 64.4, 50.5, 37.7, 35.5, 32.5, 28.6, 28.5, 22.4, 21.1.

FT-IR (film): 3354, 2943, 1732, 1520, 1366, 1244, 1174, 1043, 702 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{20}H_{32}NO_4$: 350.2326, found: 350.2327.

$[\alpha]^{23}_{D}$ = +15.4 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (8-fluoro-1-phenyloctan-3-yl)carbamate (60).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-10**. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 152 mg, 78% yield, 90% ee; (*R*,*R*)-**L2**: 155 mg, 80% yield, 90% ee.

After recrystallization using *n*-pentane/hexanes: (*S*,*S*)-**L2**: 139 mg, 90% ee → 119 mg, 86% yield (67% yield overall), 93% ee; (*R*,*R*)-**L2**: 101 mg, 90% ee → 79 mg, 78% yield (63% yield overall), 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 7.7 min (minor), 10.5 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 2H), 7.23 – 7.13 (m, 3H), 4.43 (dt, *J* = 47.3, 6.1 Hz, 2H), 4.32 – 4.28 (m, 1H), 3.63 (s, 1H), 2.76 – 2.56 (m, 2H), 1.87 – 1.58 (m, 4H), 1.56 – 1.31 (m, 15H).

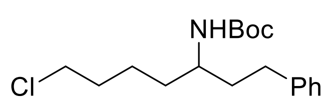
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 142.2, 128.51, 128.48, 126.0, 84.2 (d, J = 164 Hz), 79.1, 50.6, 37.8, 35.8, 32.6, 30.5 (d, J = 19.5 Hz), 28.6, 25.6, 25.3 (d, J = 5.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ –218.1.

FT-IR (film): 3347, 2936, 1702, 1508, 1364, 1246, 1168, 1043, 699 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{19}H_{31}FNO_2$: 324.2333, found: 324.2331.

$[\alpha]^{23}_{D}$ = +12.6 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (7-chloro-1-phenylheptan-3-yl)carbamate (61).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-11**. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 160 mg, 82% yield, 90% ee; (*R*,*R*)-**L2**: 165 mg, 85% yield, 90% ee.

After recrystallization using *n*-pentane/hexanes: (*S*,*S*)-**L2**: 148 mg, 90% ee → 95 mg, 64% yield (53% yield overall), 96% ee; (*R*,*R*)-**L2**: 119 mg, 90% ee → 83 mg, 70% yield (59% yield overall), 96% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 10.5 min (minor), 12.0 min (major).

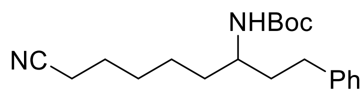
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 4.31 (d, *J* = 9.4 Hz, 1H), 3.64 (s, 1H), 3.54 – 3.50 (m, 2H), 2.77 – 2.57 (m, 2H), 1.87 – 1.60 (m, 4H), 1.55 – 1.36 (m, 13H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 142.1, 128.53, 128.47, 126.0, 79.2, 50.4, 45.1, 37.6, 35.1, 32.5, 32.5, 28.6, 23.3.

FT-IR (film): 3340, 2943, 1690, 1511, 1365, 1248, 1168, 682 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{18}H_{29}ClNO_2$: 326.1881, found: 326.1888.

$[\alpha]^{23}_{D}$ = +1.9 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl (8-cyano-1-phenyloctan-3-yl)carbamate (62).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-12**. The product was purified by column chromatography on silica gel (3:7 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L2**: 165 mg, 83% yield, 82% ee; (*R*,*R*)-**L2**: 172 mg, 87% yield, 82% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OD column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 5.5 min (minor), 7.8 min (major).

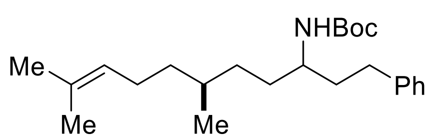
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 2H), 7.15 – 7.06 (m, 3H), 4.23 (d, *J* = 9.4 Hz, 1H), 3.54 (s, 1H), 2.68 – 2.49 (m, 2H), 2.25 (t, *J* = 7.2 Hz, 2H), 1.77 – 1.51 (m, 4H), 1.44 – 1.25 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 142.0, 134.4, 128.51, 128.45, 126.0, 123.6, 119.9, 79.2, 50.4, 37.7, 35.7, 32.5, 28.5, 25.5, 25.2.

FT-IR (film): 3350, 2935, 1690, 1517, 1365, 1247, 1170, 698 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{20}H_{31}N_2O_2$: 331.2380, found: 331.2382.

$[\alpha]^{23}_{D}$ = +7.7 (*c* 1.0, $CHCl_3$); 82% ee, from (*S*,*S*)-**L2**.



***tert*-Butyl ((6*S*)-6,10-dimethyl-1-phenylundec-9-en-3-yl)carbamate (63, 64).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-15**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L2**: 185 mg, 83% yield, 5:95 d.r.; (*R*,*R*)-**L2**: 177 mg, 79% yield, 95:5 d.r.

HPLC analysis: The d.r. was determined via HPLC on a CHIRALPAK AD column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 5.7 min (major), 6.7 min (minor).

NMR data for the product from (*S*,*S*)-**L2**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 2H), 7.17 – 7.09 (m, 3H), 5.09 – 5.00 (m, 1H), 4.26 (d, *J* = 9.3 Hz, 1H), 3.56 (s, 1H), 2.71 – 2.52 (m, 2H), 2.00 – 1.83 (m, 2H), 1.79 – 1.69 (m, 1H), 1.64 (s, 3H), 1.56 (s, 3H), 1.48 – 1.21 (m, 15H), 1.20 – 1.04 (m, 2H), 0.82 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 142.3, 131.2, 128.5, 125.9, 125.0, 109.8, 79.0, 51.0, 37.8, 37.2, 33.1, 32.5, 28.6, 25.9, 25.7, 25.1, 22.5, 19.6, 17.8.

NMR data for the product from (*R*,*R*)-**L2**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 5.14 – 5.04 (m, 1H), 4.30 (d, *J* = 9.4 Hz, 1H), 3.61 (s, 1H), 2.76 – 2.56 (m, 2H), 2.04 – 1.87 (m, 2H), 1.86 – 1.75 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.47 – 1.29 (m, 15H), 1.20 – 1.07 (m, 2H), 0.87 (d, *J* = 6.4 Hz, 3H).

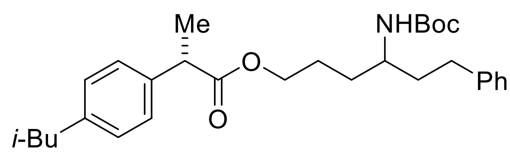
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 142.3, 131.3, 128.5, 125.9, 125.0, 109.8, 79.1, 51.0, 38.2, 37.6, 37.1, 33.3, 33.0, 32.6, 28.6, 25.9, 25.7, 19.7, 17.8.

FT-IR (film): 3346, 2963, 1691, 1524, 1454, 1365, 1247, 1167, 698 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{24}H_{40}NO_2$: 374.3054, found: 374.3052.

$[\alpha]^{23}_{D}$ = +15.1 (*c* 1.0, $CHCl_3$); 5:95 d.r., from (*S*,*S*)-**L2**.

$[\alpha]^{23}_{D}$ = +6.0 (*c* 1.0, $CHCl_3$); 95:5 d.r., from (*R*,*R*)-**L2**.



4-((*tert*-Butoxycarbonyl)amino)-6-phenylhexyl (2*S*)-2-(4-isobutylphenyl)propanoate (65, 66). The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-24**. The product was purified by column chromatography on silica gel (15:85 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 233 mg, 81% yield, 5:95 d.r.; (*R*,*R*)-**L2**: 240 mg, 83% yield, 95:5 d.r.

HPLC analysis: The d.r. was determined via HPLC on a CHIRALPAK IC column (7% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 10.0 min (minor), 12.3 min (major).

NMR data for the product from (*S*,*S*)-**L2**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.27 – 7.18 (m, 5H), 7.15 – 7.10 (m, 2H), 4.22 (d, *J* = 9.5 Hz, 1H), 4.17 – 4.02 (m, 2H), 3.72 (q, *J* = 7.1 Hz, 1H), 3.65 – 3.55 (m, 1H), 2.74 – 2.55 (m, 2H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.94 – 1.81 (m, 1H), 1.78 – 1.58 (m, 4H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.51 – 1.21 (m, 11H), 0.93 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 155.8, 142.0, 140.6, 138.0, 129.4, 128.5, 128.4, 127.3, 126.0, 79.2, 64.5, 50.3, 45.3, 45.1, 37.8, 32.5, 32.0, 30.3, 28.6, 25.3, 22.5, 18.5.

NMR data for the product from (*R*,*R*)-**L2**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.27 – 7.18 (m, 5H), 7.16 – 7.10 (m, 2H), 4.22 (d, *J* = 9.5 Hz, 1H), 4.16 – 4.04 (m, 2H), 3.72 (q, *J* = 7.1 Hz, 1H), 3.65 – 3.56 (m, 1H), 2.74 –

2.55 (m, 2H), 2.47 (d, J = 7.2 Hz, 2H), 1.94 – 1.81 (m, 1H), 1.77 – 1.57 (m, 4H), 1.53 (d, J = 7.2 Hz, 3H), 1.51 – 1.20 (m, 11H), 0.93 (d, J = 6.6 Hz, 6H).

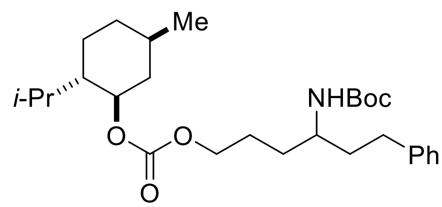
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 155.8, 142.0, 140.6, 138.0, 129.4, 128.5, 128.4, 127.3, 126.0, 79.2, 64.5, 50.3, 45.3, 45.1, 37.8, 32.5, 32.0, 30.3, 28.6, 25.3, 22.5, 18.5.

FT-IR (film): 3368, 2953, 1714, 1514, 1366, 1246, 1173, 700 cm^{-1}.

LC-MS (ESI-MS) m/z [M+Na]$^+$ calcd for $C_{30}H_{43}NNaO_4$: 504.3, found: 504.3.

$[\alpha]^{23}_D$ = +15.6 (c 1.0, $CHCl_3$); 5:95 d.r., from (S,S)-**L2**.

$[\alpha]^{23}_D$ = +22.3 (c 1.0, $CHCl_3$); 95:5 d.r., from (R,R)-**L2**.



***tert*-Butyl (6-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)oxy)-1-phenylhexan-3-yl)carbamate (67, 68).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-25**. The product was purified by column chromatography on silica gel (15:85 EtOAc/hexanes). White solid.

(S,S)-**L2**: 242 mg, 85% yield, 6:94 d.r.; (R,R)-**L2**: 236 mg, 83% yield, 95:5 d.r.

HPLC analysis: The d.r. was determined via HPLC on a CHIRALPAK IC column (7% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (S,S)-**L2**: 6.6 min (minor), 8.2 min (major).

NMR data for the product from (S,S)-**L2**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.14 (m, 3H), 4.51 (td, J = 10.9, 4.4 Hz, 1H), 4.31 (d, J = 9.4 Hz, 1H), 4.12 (t, J = 6.6 Hz, 2H), 3.71 – 3.45 (m, 1H), 2.75 – 2.56 (m, 2H), 2.13 – 2.02 (m, 1H), 2.01 – 1.89 (m, 1H), 1.80 – 1.57 (m, 7H), 1.50 – 1.35 (m, 12H), 1.13 – 0.97 (m, 2H), 0.96 – 0.84 (m, 7H), 0.78 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 155.1, 142.0, 128.53, 128.45, 126.0, 79.2, 78.4, 67.6, 50.4, 47.1, 40.9, 37.8, 34.2, 32.5, 31.5, 28.5, 26.2, 25.5, 23.4, 22.1, 20.8, 16.4.

NMR data for the product from (R,R)-**L2**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.14 (m, 3H), 4.51 (td, J = 10.9, 4.4 Hz, 1H), 4.29 (d, J = 9.5 Hz, 1H), 4.12 (t, J = 6.4 Hz, 2H), 3.68 – 3.45 (m, 1H), 2.75 – 2.56 (m, 2H), 2.11 – 2.02 (m, 1H), 2.02 – 1.90 (m, 1H), 1.82 – 1.56 (m, 7H), 1.51 – 1.35 (m, 12H), 1.13 – 0.97 (m, 2H), 0.94 – 0.83 (m, 7H), 0.79 (d, J = 7.0 Hz, 3H).

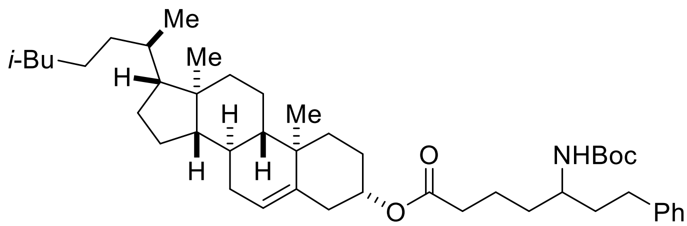
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 155.1, 142.0, 128.55, 128.47, 126.0, 79.3, 78.4, 67.6, 50.4, 47.1, 40.9, 37.9, 34.2, 32.5, 32.2, 31.5, 28.6, 26.2, 25.5, 23.4, 22.1, 20.9, 16.4.

FT-IR (film): 3357, 2953, 1738, 1515, 1454, 1366, 1262, 1174, 959, 699 cm^{-1}.

LC-MS (ESI-MS) m/z [M+Na]$^+$ calcd for $C_{28}H_{45}NNaO_5$: 498.3, found: 498.3.

$[\alpha]^{23}_D$ = –26.5 (c 1.0, $CHCl_3$); 6:94 d.r., from (S,S)-**L2**.

$[\alpha]^{23}_D$ = –27.6 (c 1.0, $CHCl_3$); 95:5 d.r., from (R,R)-**L2**.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 5-((tert-butoxycarbonyl)amino)-7-phenylheptanoate (69, 70). The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-16**. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 358 mg, 87% yield, 16:84 d.r.; (*R*,*R*)-**L2**: 343 mg, 83% yield, 84:16 d.r.

After recrystallization using *n*-pentane/hexanes: (*R*,*R*)-**L2**: 199 mg, 84:16 d.r. → 101 mg, 51% yield (42% yield overall), >99:1 d.r.

HPLC analysis: The d.r. was determined via HPLC on a CHIRALPAK IC column (7% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 8.9 min (minor), 14.6 min (major).

NMR data for the product from (*S*,*S*)-**L2**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 2H), 7.28 – 7.22 (m, 3H), 5.47 – 5.42 (m, 1H), 4.74 – 4.62 (m, 1H), 4.46 (d, *J* = 9.3 Hz, 1H), 3.78 – 3.66 (m, 1H), 2.83 – 2.63 (m, 2H), 2.41 – 2.32 (m, 4H), 2.13 – 1.86 (m, 6H), 1.78 – 1.39 (m, 26H), 1.27 – 1.05 (m, 12H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.95 (dd, *J* = 6.6, 1.9 Hz, 6H), 0.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 155.8, 142.0, 139.7, 128.5, 128.4, 125.9, 122.7, 79.1, 73.9, 56.8, 56.2, 50.1, 42.4, 39.8, 39.6, 38.2, 37.6, 37.1, 36.7, 36.3, 35.9, 35.0, 34.4, 32.5, 32.0, 31.9, 28.5, 28.3, 28.1, 27.9, 24.4, 23.9, 22.9, 22.7, 21.4, 21.1, 19.4, 18.8, 11.9.

NMR data for the product from (*R*,*R*)-**L2**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, *J* = 8.2, 6.8 Hz, 2H), 7.28 – 7.20 (m, 3H), 5.48 – 5.41 (m, 1H), 4.75 – 4.63 (m, 1H), 4.48 (d, *J* = 9.3 Hz, 1H), 3.75 – 3.66 (m, 1H), 2.88 – 2.63 (m, 2H), 2.42 – 2.31 (m, 4H), 2.19 – 1.85 (m, 6H), 1.82 – 1.39 (m, 26H), 1.28 – 1.06 (m, 12H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.95 (dd, *J* = 6.7, 1.8 Hz, 6H), 0.76 (s, 3H).

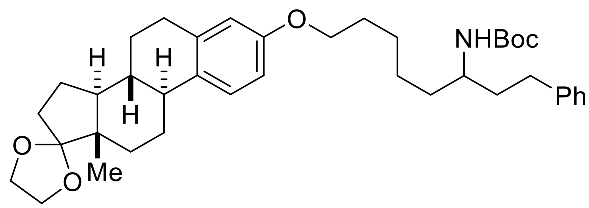
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 155.7, 142.0, 139.7, 128.43, 128.40, 125.9, 122.7, 79.0, 73.9, 56.7, 56.2, 50.1, 42.4, 39.8, 39.6, 38.2, 37.6, 37.1, 36.6, 36.3, 35.9, 35.0, 34.4, 32.5, 32.0, 31.9, 28.5, 28.3, 28.1, 27.9, 24.4, 23.9, 22.9, 22.7, 21.4, 21.1, 19.4, 18.8, 11.9.

FT-IR (film): 3368, 2941, 1722, 1366, 1248, 1174, 759 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{45}H_{72}NO_4$: 690.5456, found: 690.5451.

$[\alpha]^{23}_D$ = –18.7 (*c* 1.0, $CHCl_3$); 16:84 d.r., from (*S*,*S*)-**L2**.

$[\alpha]^{23}_D$ = –36.2 (*c* 1.0, $CHCl_3$); 84:16 d.r., from (*R*,*R*)-**L2**.



***tert*-Butyl (8-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)-1-phenyloctan-3-yl)carbamate (71, 72).** The title compound was synthesized according to **GP-6** from 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate and **Zn-17**. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 312 mg, 84% yield, 8:92 d.r.; (*R*,*R*)-**L2**: 327 mg, 88% yield, 94:6 d.r.

HPLC analysis: The d.r. was determined via HPLC on a CHIRALPAK AD column (7% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 10.8 min (minor), 11.9 min (major).

NMR data for the product from (*S*,*S*)-**L2**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 2H), 7.19 – 7.10 (m, 4H), 6.65 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.58 (d, *J* = 2.8 Hz, 1H), 4.28 (d, *J* = 9.4 Hz, 1H), 3.98 – 3.81 (m, 6H), 3.64 – 3.56 (m, 1H), 2.88 – 2.74 (m, 2H), 2.70 – 2.49 (m, 2H), 2.33 – 2.14 (m, 2H), 2.08 – 1.92 (m, 1H), 1.90 – 1.67 (m, 7H), 1.67 – 1.55 (m, 2H), 1.55 – 1.24 (m, 20H), 0.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 155.8, 142.2, 138.1, 132.7, 128.49, 128.46, 126.4, 125.9, 119.6, 114.5, 112.1, 79.1, 67.8, 65.4, 64.7, 50.7, 49.5, 46.3, 43.7, 39.2, 37.7, 35.8, 34.4, 32.5, 30.9, 29.9, 29.4, 28.6, 27.1, 26.3, 26.2, 25.8, 22.5, 14.5.

NMR data for the product from (*R*,*R*)-**L2**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 2H), 7.16 – 7.12 (m, 4H), 6.65 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.58 (d, *J* = 2.7 Hz, 1H), 4.27 (d, *J* = 9.4 Hz, 1H), 4.01 – 3.81 (m, 6H), 3.66 – 3.53 (m, 1H), 2.89 – 2.72 (m, 2H), 2.72 – 2.52 (m, 2H), 2.34 – 2.14 (m, 2H), 2.05 – 1.94 (m, 1H), 1.90 – 1.67 (m, 7H), 1.67 – 1.55 (m, 2H), 1.54 – 1.28 (m, 20H), 0.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 155.8, 142.2, 138.1, 132.7, 128.49, 128.47, 126.4, 125.9, 119.6, 114.5, 112.1, 79.1, 67.8, 65.4, 64.7, 50.7, 49.5, 46.3, 43.8, 39.2, 37.7, 35.8, 34.4, 32.5, 30.9, 29.9, 29.4, 28.6, 27.1, 26.3, 26.2, 25.8, 22.5, 14.5.

FT-IR (film): 3356, 2937, 1698, 1498, 1255, 1165, 1044, 754 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{39}H_{56}NO_5$: 618.4153, found: 618.4158.

$[\alpha]^{23}_D$ = +40.4 (*c* 1.0, $CHCl_3$); 8:92 d.r., from (*S*,*S*)-**L2**.

$[\alpha]^{23}_D$ = +23.2 (*c* 1.0, $CHCl_3$); 94:6 d.r., from (*R*,*R*)-**L2**.

VI. Effect of Reaction Parameters

General Procedure 8 (GP-8).

Preparation of a solution of the catalyst: In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a stir bar was charged with $NiBr_2$·glyme (3.1 mg, 0.010 mmol, 10 mol%) and (*S*,*S*)-**L1** (10.9 mg, 0.012 mmol, 12 mol%). Next, THF (1.0 mL) was added, the vial was capped with a PTFE septum cap, and the mixture was stirred at room temperature for 30 min, leading to an orange, homogeneous solution.

Cross-coupling: In a nitrogen-filled glovebox, a solution of the electrophile (0.10 mmol, 1.0 equiv) in THF (1.0 mL) was added to the reaction mixture. The vial was capped with a PTFE septum cap and taken out of the glovebox. The reaction vial was then placed in an *i*-PrOH cooling bath at 0 °C, and the reaction mixture was stirred at 0 °C for 10 min. Then, the alkylzinc solution (0.11 mmol, 1.1 equiv) was added dropwise via microsyringe over 3 min, during which the reaction mixture turned dark. The punctures on the septum cap were sealed with grease, and the mixture was stirred at 0 °C for 36 h.

Work-up: The reaction was quenched at 0 °C by the addition of MeOH (0.1 mL). *n*-Dodecane (23 μL, 0.10 mmol, 1.0 equiv) was added as an internal standard. The reaction mixture was passed through a short pad of silica gel, with Et_2O as the eluent. The solvent was removed under reduced pressure, and the residue was purified by chromatography.

General Procedure 9 (GP-9).

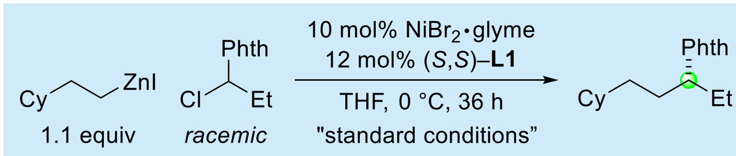
Preparation of a solution of the catalyst: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was equipped with a stir bar and charged with $NiBr_2$·glyme (1.5 mg, 0.0050 mmol, 5.0 mol%), (*R*,*R*)-**L2** (1.8 mg, 0.0060 mmol, 6.0 mol%), and LiCl (8.5 mg, 0.20 mmol, 2.0 equiv). Next, THF (0.4 mL) was added, the vial was capped with a PTFE septum cap, and the mixture was stirred at room temperature for 30 min, during which it became a light-green, homogeneous solution.

Cross-coupling: In a nitrogen-filled glovebox, DMAP (0.050 mmol, 0.50 equiv), the NHP ester (0.10 mmol, 1.0 equiv), and TMSCl (0.080 mmol, 0.80 equiv) were added sequentially to the reaction mixture as stock solutions in THF, totaling 1.2 mL THF (including 0.4 mL from the catalyst solution). The vial was sealed with a septum cap and wrapped with electrical tape. Next, the vial was removed from the glovebox and cooled to 0 °C using an *i*-PrOH cooling bath. After the white, heterogeneous reaction mixture had stirred at 0 °C for 10 min, the alkylzinc solution (0.12 mmol, 1.2 equiv) was added dropwise via microsyringe, resulting in a yellow, homogeneous solution. The punctures on the septum cap were sealed with grease, and the mixture was stirred at 0 °C for 18 h.

Work-up: The reaction was quenched at 0 °C by the addition of MeOH (0.1 mL). The resulting mixture was allowed to warm to room temperature, and then 1-indanone (2.6 mg, 0.020 mmol) was added as an internal standard. The mixture was filtered through a small plug of silica gel, which was flushed with Et_2O (10 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by chromatography.

Table S-1: 2-(1-Chloropropyl)isoindoline-1,3-dione was reacted with **Zn-1** according to **GP-8**. The yields were determined via GC analysis, with *n*-dodecane as the internal standard. The ee values were determined via SFC analysis after purification by preparative thin-layer chromatography. All data are the average of two experiments.

Table S-1. Effect of Reaction Parameters: An Alkyl Chloride as the Electrophile.



entry	variation from the "standard conditions"	yield (%)[a]	ee (%)[b]
1	none	90	92
2	no $NiBr_2$•glyme	<1	–
3	no (*S*,*S*)–**L1**	<1	–
4	**L2**, instead of (*S*,*S*)–**L1**	32	16
5	**L3**, instead of (*S*,*S*)–**L1**	81	84
6	**L4**, instead of (*S*,*S*)–**L1**	13	22
7	**L5**, instead of (*S*,*S*)–**L1**	19	41
8	**L6**, instead of (*S*,*S*)–**L1**	19	3
9	2-MeTHF, instead of THF	96	91
10	MTBE, instead of THF	81	70
11	1,4-dioxane, instead of THF	48	86
12	DME, instead of THF	15	90
13	0.1 M, instead of 0.05 M	94	91
14	5.0 mol% $NiBr_2$•glyme, 6.0 mol% (*S*,*S*)–**L1**	79	91
15	RZnBr, instead of RZnI	78	88
16	1.0 equiv alkylzinc	81	92
17	9 h, instead of 36 h	70	92
18	18 h, instead of 36 h	86	92
19	r.t., instead of 0 °C	98	90
20	0.05 equiv H_2O added	31	92
21	0.10 equiv H_2O added	11	92
22	1 mL air added with syringe	64	91
23	1 mL air added with syringe (72 h)	77	91
24	under air in a closed vial	50	91

All data are the average of two experiments. [a] Determined through GC analysis. [b] Determined through SFC analysis.

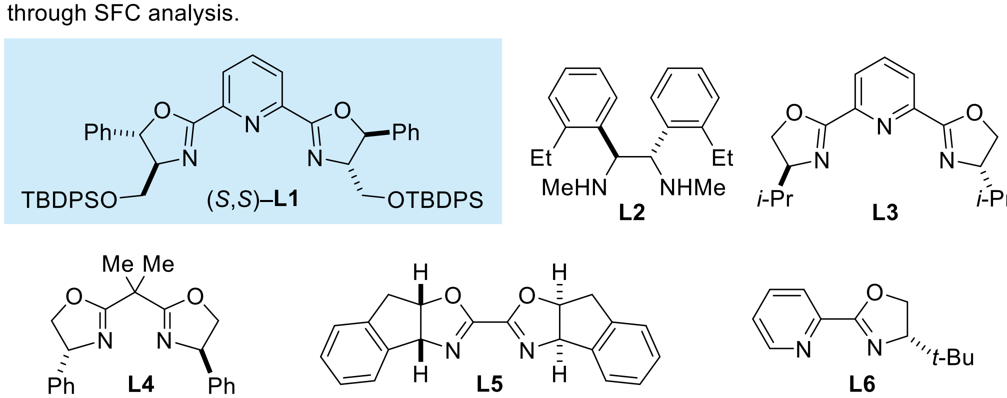
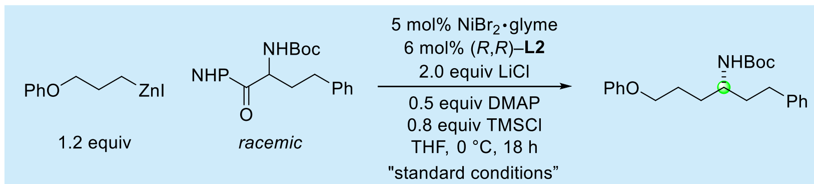


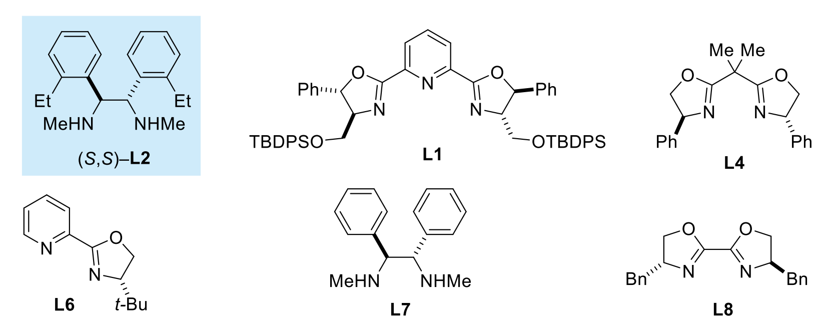
Table S-2: 1,3-Dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate was reacted with **Zn-18** according to **GP-9**. The yields were determined via LC-MS analysis, with 1-indanone as the internal standard. The ee values were determined via HPLC analysis after purification by preparative thin layer chromatography. All data are the average of two experiments.

Table S-2. Effect of Reaction Parameters: An Alkyl NHP Ester as the Coupling Partner.



entry	variation from the "standard conditions"	yield (%)[a]	ee (%)[b]
1	none	79	91
2	no $NiBr_2$•glyme	<1	–
3	no (*S*,*S*)–**L2**	30	<2
4	no LiCl	16	88
5	no DMAP	70	65
6	no TMSCl	65	87
7	**L1**, instead of (*S*,*S*)–**L2**	14	31
8	**L4**, instead of (*S*,*S*)–**L2**	9	6
9	**L6**, instead of (*S*,*S*)–**L2**	30	16
10	**L7**, instead of (*S*,*S*)–**L2**	74	86
11	**L8**, instead of (*S*,*S*)–**L2**	43	3
12	LiF, instead of LiCl	15	89
13	LiBr, instead of LiCl	64	87
14	LiI, instead of LiCl	50	90
15	NaCl, instead of LiCl	17	90
16	KCl, instead of LiCl	19	89
17	CsCl, instead of LiCl	32	83
18	$N(n\text{-}Bu)_4Cl$, instead of LiCl	25	87
19	pyridine, instead of DMAP	79	87
20	2.5 mol% $NiBr_2$•glyme, 3.0 mol% (*S*,*S*)–**L2**	65	88
21	RZnBr, instead of RZnI	82	82
22	1.0 equiv alkylzinc	67	89
23	9 h, instead of 18 h	70	90
24	r.t., instead of 0 °C	70	82
25	0.12 M, instead of 0.07 M	50	90
26	0.04 M, instead of 0.07 M	78	90
27	DME, instead of THF	51	77
28	MTBE, instead of THF	17	84
29	0.05 equiv H_2O added	73	88
30	0.10 equiv H_2O added	70	87
31	1 mL air added with syringe	71	88
32	under air in a closed vial	20	82

All data are the average of two experiments. [a] Determined through LC/MS analysis. [b] Determined through HPLC analysis.

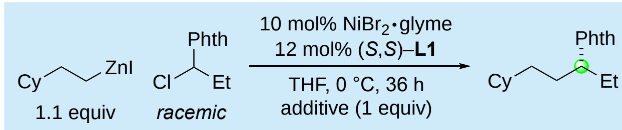


VII. Studies of Functional-Group Compatibility

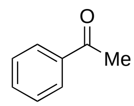
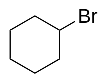
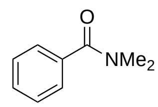
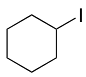
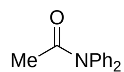
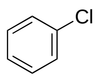
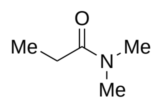
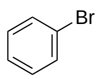
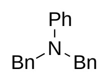
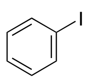
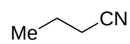
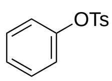
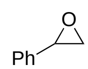
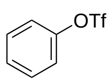
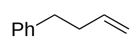
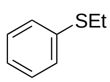
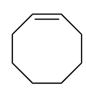
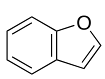
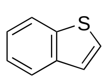
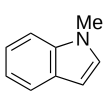
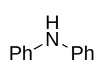
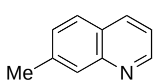
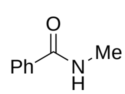
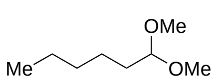
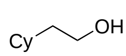
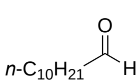
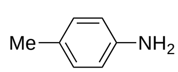
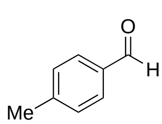
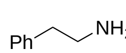
Table S-3: 2-(1-Chloropropyl)isoindoline-1,3-dione was reacted with **Zn-1** according to **GP-8**, in the presence of 1.0 equiv of the additives shown below. The additive was added after the addition of the 2-(1-chloropropyl)isoindoline-1,3-dione solution. The yield of the coupling product and the percent recovery of the additive were determined via GC analysis, with *n*-dodecane as the internal standard. The ee values were determined via SFC analysis after purification by preparative thin-layer chromatography. All data are the average of two experiments.

Table S-4: 1,3-Dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate was reacted with **Zn-18** according to **GP-9**, in the presence of 1.0 equiv of the additives shown below. The additive was added before TMSCl. In addition to 1-indanone (2.6 mg, 0.020 mmol), *n*-dodecane (23 μL, 0.10 mmol) was added as an internal standard after quenching the reaction. The yields were determined via LC-MS analysis, with 1-indanone as the internal standard. The percent recoveries of the additives were determined via GC analysis, with *n*-dodecane as the internal standard. The ee values were determined via HPLC analysis after purification by preparative thin-layer chromatography. All data are the average of two experiments.

Table S-3. Functional-Group Compatibility: An Alkyl Chloride as the Electrophile.

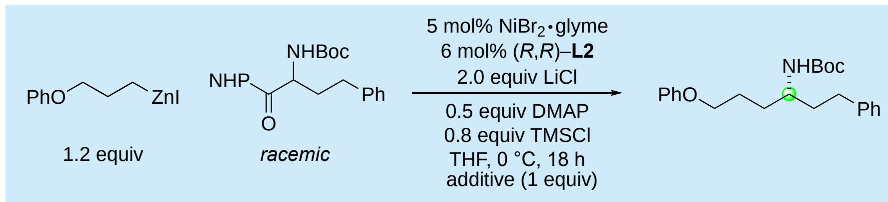


without additive: 90% yield, 92% ee

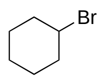
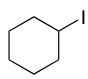
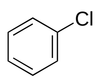
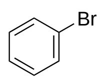
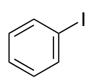
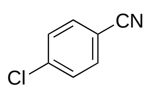
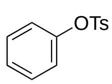
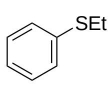
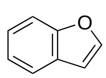
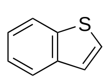
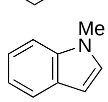
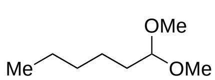
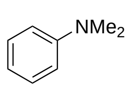
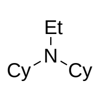
additive; recovery (%) [a]		yield (%) [a]	ee (%) [b]	additive; recovery (%) [a]		yield (%) [a]	ee (%) [b]
n-$C_{10}H_{21}Cl$	>95	87	91		>95	88	91
	>95	84	91		>95	93	91
	>95	89	91		>95	89	91
	>95	84	91		>95	89	92
	>95	86	91		92	84	91
	>95	87	91		>95	85	92
	>95	87	91		>95	82	91
	>95	87	91		>95	80	91
	>95	89	91		>95	82	81
	>95	87	91	n-Bu—≡—n-Bu	>95	85	91
	>95	83	91	Ph—≡—Ph	>95	88	91
	>95	78	90		>95	88	92
	>95	84	92		>95	92	92
	>95	87	92		92 [c]	93	91
	>95	84	92		**67**	**14**	85
	>95	83	91		**30**	**45**	81

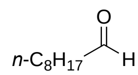
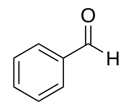
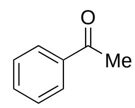
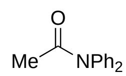
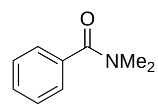
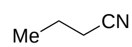
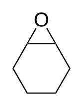
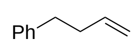
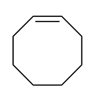
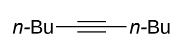
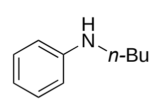
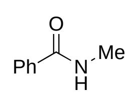
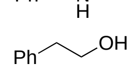
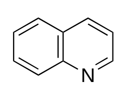
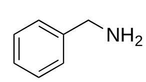
[a] Determined through GC analysis. [b] Determined through SFC analysis. [c] 2.2 equiv of alkylzinc was used instead.

Table S-4. Functional-Group Compatibility: An NHP Ester as the Coupling Partner.



without additive: 79% yield, 91% ee

additive; recovery (%) [a]		yield (%) [b]	ee (%) [c]
n-$C_{10}H_{21}Cl$	>95	85	90
	>95	85	91
	>95	86	90
	>95	86	90
	>95	83	90
	>95	73	91
	>95	88	90
	>95	82	90
	>95	82	90
	>95	81	90
	>95	79	90
	>95	90	91
	>95	85	89
	>95	89	90
	>95	84	90

additive; recovery (%) [a]		yield (%) [b]	ee (%) [c]
	>95	71	90
	90	90	90
	>95	88	91
	>95	80	89
	90	88	90
	85	91	89
	70	85	90
	>95	81	90
	>95	81	90
	85	87	90
	>95	83	90
	>95	80	90
	>95 [d]	79	86
	50	30	90
	0	18	88

[a] Determined through GC analysis. [b] Determined through LC-MS analysis. [c] Determined through HPLC analysis.
[d] 2.4 equiv of alkylzinc, 4.0 equiv LiCl, and 2.5 equiv TMSCl were used. The additive was recovered as the TMS ether.

VIII. One-Pot Reactions

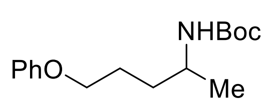
General Procedure 10 (GP-10).

Preparation of the NHP ester: In the air, *N*-hydroxyphthalimide (97.9 mg, 0.60 mmol, 1.0 equiv), the Boc-protected amino acid (0.60 mmol, 1.0 equiv), and DMAP (36.7 mg, 0.30 mmol, 0.50 equiv) were added sequentially to an oven-dried 40 mL vial equipped with a cross-type stir bar. The vial was capped with a PTFE septum cap and wrapped with electric tape. The reaction vial was evacuated and back-filled with nitrogen (four cycles), after which a nitrogen-filled balloon was attached. THF (2.8 mL) was added via syringe, and the mixture was allowed to stir for 10 min, leading to an orange, heterogeneous mixture. *N*,*N'*-diisopropylcarbodiimide (112 μL, 0.72 mmol, 1.20 equiv) was then added dropwise via microsyringe over 2 min. The mixture was stirred at room temperature for 1 h.

Preparation of a solution of the catalyst: In the air, $NiBr_2$·glyme (9.3 mg, 0.030 mmol, 5.0 mol%), (*R*,*R*)-**L2** (10.7 mg, 0.036 mmol, 6.0 mol%), and anhydrous LiCl (52.1 mg, 1.20 mmol, 2.00 equiv; because LiCl is hygroscopic, it is recommended to weigh the compound in a capped 4 mL vial in a glovebox, transfer the vial out of the glovebox, and pour the compound into the reaction vial) were added sequentially to an oven-dried 40 mL vial equipped with a cross-type stir bar. The vial was then capped with a PTFE septum cap and wrapped with electrical tape. The vial was evacuated and back-filled with nitrogen (four cycles), after which a nitrogen-filled balloon was attached. THF (4.0 mL) was added via syringe, and the mixture was allowed to stir for 30 min, during which it became a light-green, homogeneous solution.

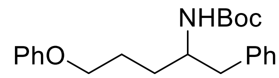
Cross-coupling: The catalyst solution (4.0 mL) was transferred via syringe to the reaction vial containing the NHP ester, leading to an orange, homogeneous solution. The vial was washed with THF (0.5 mL), which was also added to the reaction vial. Next, TMSCl (61 μL, 0.48 mmol, 0.80 equiv) was added via microsyringe, leading to a colorless, opaque mixture. The reaction vial was then placed in an isopropanol cooling bath at 0 °C, and the mixture was stirred at 0 °C for 10 min. Then, the alkylzinc solution (0.72 mmol, 1.2 equiv) was added dropwise via syringe over 5 min, during which the reaction mixture became yellow and homogeneous. The balloon was removed, and the septum cap was sealed with grease. The mixture was stirred at 0 °C for 18 h.

Work-up: The reaction was quenched with methanol (0.2 mL), and the mixture was passed through a plug of silica gel; the vial, the cap, and the silica gel were rinsed with Et_2O. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel.



***tert*-Butyl (5-phenoxypentan-2-yl)carbamate (36).** The title compound was synthesized according to **GP-10** from (*tert*-butoxycarbonyl)alanine and **Zn-18**. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). White solid.

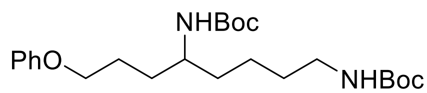
(S,S)-**L2**: 112 mg, 67% yield, 90% ee; (R,R)-**L2**: 106 mg, 63% yield, 90% ee.



***tert*-Butyl (5-phenoxy-1-phenylpentan-2-yl)carbamate (42).** The title compound was synthesized according to **GP-10** from (*tert*-butoxycarbonyl)phenylalanine and **Zn-18**. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes). White solid.

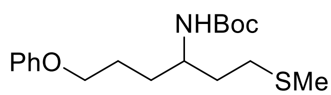
(S,S)-**L2**: 135 mg, 63% yield, 90% ee; (R,R)-**L2**: 131 mg, 61% yield, 90% ee.

After recrystallization using *n*-pentane/hexanes: (S,S)-**L2**: 112 mg, 90% ee → 95 mg, 85% yield (53% yield overall), >99% ee; (R,R)-**L2**: 111 mg, 90% ee → 96 mg, 86% yield (53% yield overall), >99% ee.



Di-*tert*-butyl (8-phenoxyoctane-1,5-diyl)dicarbamate (43). The title compound was synthesized according to **GP-10** from N^2,N^6-bis(*tert*-butoxycarbonyl)lysine and **Zn-18**. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes). White solid.

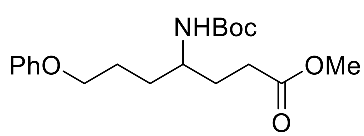
(S,S)-**L2**: 170 mg, 65% yield, 90% ee; (R,R)-**L2**: 152 mg, 58% yield, 90% ee.



***tert*-Butyl (1-(methylthio)-6-phenoxyhexan-3-yl)carbamate (44).** The title compound was synthesized according to **GP-10** from (*tert*-butoxycarbonyl)methionine and **Zn-18**. The product was purified by column chromatography on silica gel (3:7 EtOAc/hexanes). White solid.

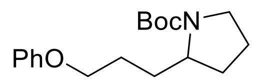
(S,S)-**L2**: 105 mg, 52% yield, 92% ee; (R,R)-**L2**: 105 mg, 52% yield, 92% ee.

After recrystallization using *n*-pentane/hexanes: (S,S)-**L2**: 76 mg, 92% ee → 56 mg, 74% yield (38% yield overall), >99% ee; (R,R)-**L2**: 82 mg, 92% ee → 68 mg, 83% yield (43% yield overall), >99% ee.



Methyl 4-((*tert*-butoxycarbonyl)amino)-7-phenoxyheptanoate (47). The title compound was synthesized according to **GP-10** from 2-((*tert*-butoxycarbonyl)amino)-5-methoxy-5-oxopentanoic acid and **Zn-18**. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes). White solid.

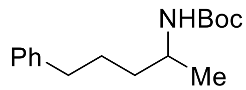
(S,S)-**L2**: 110 mg, 52% yield, 91% ee; (R,R)-**L2**: 107 mg, 51% yield, 92% ee.



***tert*-Butyl 2-(3-phenoxypropyl)pyrrolidine-1-carboxylate (48).** The title compound was synthesized according to **GP-10** from (*tert*-butoxycarbonyl)proline and **Zn-18**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). White solid.

(*S*,*S*)-**L2**: 102 mg, 56% yield, 90% ee; (*R*,*R*)-**L2**: 105 mg, 57% yield, 90% ee.

IX. Applications



***tert*-Butyl (5-phenylpentan-2-yl)carbamate (73).** The title compound was synthesized according to **GP-10** from (*tert*-butoxycarbonyl)-*L*-alanine and **Zn-21**. The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes). White solid. The analytical data matched a literature report.[5]

(*S*,*S*)-**L2**: 196 mg, 62% yield, 90% ee; (*R*,*R*)-**L2**: 209 mg, 66% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OJ column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 7.4 min (minor), 9.6 min (major).

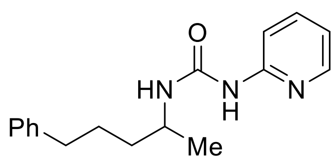
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 4.35 – 4.30 (m, 1H), 3.74 – 3.64 (m, 1H), 2.68 – 2.58 (m, 2H), 1.74 – 1.59 (m, 2H), 1.51 – 1.38 (m, 11H), 1.10 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 142.4, 128.5, 128.4, 125.8, 79.0, 46.4, 37.0, 35.8, 28.5, 28.0, 21.4.

FT-IR (film): 3340, 2932, 1704, 1504, 1366, 1248, 1174, 1079, 699 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{16}H_{25}NNaO_2$: 286.2, found: 286.1.

$[\alpha]^{23}_{D}$ = –3.4 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



1-(5-Phenylpentan-2-yl)-3-(pyridin-2-yl)urea (74). The title compound was synthesized according to a reported procedure.[6] An oven-dried 40 mL vial was equipped with a stir bar and *tert*-butyl (5-phenylpentan-2-yl)carbamate (141 mg, 0.54 mmol, 1.0 equiv), and it was then sealed with a rubber septum cap. The vial was placed under a nitrogen atmosphere by evacuating and back-filling the vial (three cycles), followed by the addition of anhydrous DCM (18 mL). 2-Chloropyridine (152 μL, 1.61 mmol, 3.0 equiv) was added, followed by trifluoromethanesulfonic anhydride (135 μL, 0.80 mmol, 1.5 equiv), and the reaction mixture was stirred at room temperature for 50 min. Then, triethylamine (448 μL, 3.21 mmol, 6.0 equiv) was added, followed by 2-aminopyridine (151 mg, 1.61 mmol, 3.0 equiv), leading to a dark red, homogeneous solution. The reaction was stirred at room temperature for 20 h. The mixture was then concentrated, and the residue was purified by column chromatography on silica gel (5:7:8 EtOAc/hexanes/DCM). Light-yellow oil.

(*S*,*S*)-**L2**: 0.69 mmol scale, 117 mg, 60% yield, 91% ee; (*R*,*R*)-**L2**: 0.54 mmol scale, 98 mg, 65% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (8% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 9.1 min (major), 11.3 min (minor).

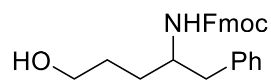
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J* = 7.8 Hz, 1H), 8.85 (s, 1H), 8.16 – 8.10 (m, 1H), 7.59 – 7.50 (m, 1H), 7.32 – 7.21 (m, 2H), 7.21 – 7.12 (m, 3H), 6.90 – 6.79 (m, 2H), 4.12 – 3.98 (m, 1H), 2.74 – 2.57 (m, 2H), 1.82 – 1.53 (m, 4H), 1.25 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 153.8, 146.0, 142.6, 138.3, 128.5, 128.4, 125.8, 116.6, 112.1, 45.8, 36.9, 35.9, 28.0, 21.6.

FT-IR (film): 3223, 3062, 1682, 1556, 1480, 1416, 1302, 1242, 777 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{17}H_{22}N_3O$: 284.2, found: 284.1.

$[\alpha]^{23}_{D}$ = +28.5 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L2**.



(9*H*-Fluoren-9-yl)methyl (5-hydroxy-1-phenylpentan-2-yl)carbamate (75). **GP-10** was applied on a 1.2 mmol scale to (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-phenylalanine and **Zn-23** to generate the Fmoc-protected amine in situ. The reaction was quenched with methanol (0.2 mL), and the mixture was passed through a short pad of silica gel, with Et_2O as the eluent (~15 mL) into a 40 mL vial. The resulting mixture was concentrated under reduced pressure to yield an orange oil.

The vial was then placed under a nitrogen atmosphere by evacuating and back-filling the vial (three cycles), followed by the addition of methanol (5.0 mL). A solution of HCl in methanol (1.25 M, 6.0 mL) was then added dropwise over 5 min. After the mixture had stirred at room temperature for 2 h, the methanol was evaporated under reduced pressure. Water (10 mL) was added to the resulting residue, and the mixture was extracted with DCM (5 mL x 3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (7:3 EtOAc/hexanes). White solid. The analytical data matched the literature report.[7]

(*S*,*S*)-**L2**: 198 mg, 41% yield, 82% ee; (*R*,*R*)-**L2**: 176 mg, 37% yield, 79% ee.

After recrystallization using THF/hexanes: (*S*,*S*)-**L2**: 198 mg, 82% ee → 136 mg, 69% yield (28% yield overall), >99% ee; (*R*,*R*)-**L2**: 176 mg, 79% ee → 128 mg, 73% yield (27% yield overall), >99% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IC column (40% i-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (S,S)-L2: 3.4 min (minor), 4.0 min (major).

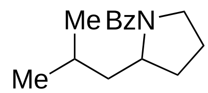
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.42 (m, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.27 – 7.18 (m, 4H), 7.15 – 7.04 (m, 3H), 4.52 (d, *J* = 9.0 Hz, 1H), 4.45 – 4.24 (m, 2H), 4.10 (t, *J* = 6.6 Hz, 1H), 3.86 (s, 1H), 3.61 – 3.37 (m, 2H), 2.78 – 2.42 (m, 2H), 1.56 – 1.45 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 144.0, 141.4, 137.7, 129.5, 128.5, 127.7, 127.0, 126.5, 125.0, 120.0, 66.3, 62.6, 51.9, 47.4, 41.4, 30.8, 29.0.

FT-IR (film): 3316, 2933, 2360, 1686, 1534, 1250, 736 cm^{-1}.

LC-MS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{26}H_{28}NO_3$: 402.2, found: 402.2.

$[\alpha]^{23}_D$ = +3.2 (c 1.0, $CHCl_3$); >99% ee, from (S,S)-**L2**.



(2-Isobutylpyrrolidin-1-yl)(phenyl)methanone. **GP-10** was applied on a 0.60 mmol scale to (*tert*-butoxycarbonyl)-*L*-proline and **Zn-4** to generate the Boc-protected amine. Next, trifluoroacetic acid (9.0 mL) was added at 0 °C, and the mixture was stirred at room temperature. The consumption of the Boc-protected amine and the formation of the deprotected pyrrolidine were monitored via ^{1}H NMR spectroscopy, using 1,3,5-trimethoxybenzene as an internal standard.

Yield by NMR of coupling and Boc-deprotection:

(S,S)-**L2**: 69% yield; (R,R)-**L2**: 74% yield.

After the reaction had stirred at room temperature for 2 h, the mixture was basified using 10% aqueous NaOH. The organic layer was separated, and the aqueous phases were extracted with DCM (10 mL x 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to ~10 mL under reduced pressure. To this solution was added triethylamine (502 μL, 3.60 mmol, 6.0 equiv) and benzoyl chloride (209 μL, 1.80 mmol, 3.0 equiv), and the reaction mixture was stirred at room temperature for 14 h. The mixture was then concentrated under reduced pressure and purified by column chromatography on silica gel (1:4 EtOAc/hexanes). The resulting light-yellow solid was extracted with hexanes to yield the product. Colorless oil.

(S,S)-**L2**: 87 mg, 62% yield, 89% ee; (R,R)-**L2**: 93 mg, 67% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IC column (25% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (S,S)-**L2**: 7.9 min (minor), 8.8 min (major).

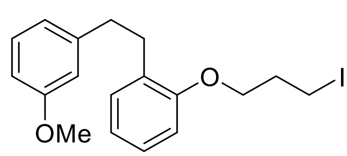
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.32 (m, 5H), 4.46 – 3.81 (m, 1H), 3.73 – 3.29 (m, 2H), 2.17 – 1.80 (m, 3H), 1.77 – 1.54 (m, 2H), 1.34 – 0.89 (m, 6H), 0.50 (dd, J = 104.9, 6.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 137.6, 129.8, 128.2, 127.4, 56.0, 49.9, 43.3, 30.7, 25.8, 25.2, 23.9, 22.0.

FT-IR (film): 2955, 2870, 1633, 1578, 1415, 1166, 703 cm^{-1}.

HRMS (ESI-MS) m/z $[M+Na]^+$ calcd for $C_{15}H_{21}NNaO$: 254.1515, found: 254.1524.

$[\alpha]^{23}_D$ = +35.9 (c 1.0, $CHCl_3$); 89% ee, from (S,S)-**L2**.



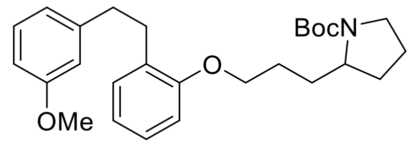
1-(3-Iodopropoxy)-2-(3-methoxyphenethyl)benzene. In the air, K_2CO_3 (2.3 g, 16.4 mmol, 1.5 equiv) was added to a solution of 2-(3-methoxyphenethyl)phenol (2.5 g, 11.0 mmol, 1.0 equiv) in DMF (30 mL) at room temperature, and the mixture was stirred at room temperature for 30 min. Next, 1,3-diiodopropane (6.3 mL, 54.8 mmol, 5.0 equiv) was added via syringe over 30 sec, and the reaction mixture was stirred at room temperature overnight. The reaction was quenched with water, and the resulting mixture was extracted with DCM (30 mL x 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (1:50 Et_2O/hexanes) to afford the product (2.4 g, 55% yield). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H), 7.15 – 7.11 (m, 1H), 6.93 – 6.85 (m, 2H), 6.82 – 6.71 (m, 3H), 4.05 (t, *J* = 5.7 Hz, 2H), 3.79 (s, 3H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.98 – 2.81 (m, 4H), 2.35 – 2.24 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 156.6, 144.1, 130.4, 130.2, 129.4, 127.4, 121.0, 120.8, 114.3, 111.3, 111.3, 67.2, 55.3, 36.6, 33.2, 32.7, 2.9.

FT-IR (film): 2922, 2590, 2351, 1600, 1468, 1239, 1165, 1044, 916, 747, 695 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M+H]$^+$ calcd for $C_{18}H_{22}IO_2$: 397.1, found: 397.0.



***tert*-Butyl 2-(3-(2-(3-methoxyphenethyl)phenoxy)propyl)pyrrolidine-1-carboxylate (77)**. The title compound was synthesized according to **GP-10** from (*tert*-butoxycarbonyl)-*L*-proline and **Zn-26** (**Zn-26** was prepared according to **GP-4**). The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L2**: 135 mg, 51% yield, 88% ee; (*R*,*R*)-**L2**: 133 mg, 51% yield, 88% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IG-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 5.0 min (minor), 6.0 min (major).

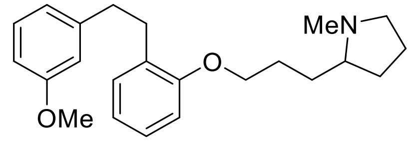
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 2H), 7.13 – 7.08 (m, 1H), 6.90 – 6.78 (m, 3H), 6.77 – 6.71 (m, 2H), 4.07 – 3.91 (m, 2H), 3.91 – 3.73 (m, 1H), 3.78 (s, 3H), 3.45 – 3.25 (m, 2H), 2.96 – 2.79 (m, 4H), 2.04 – 1.74 (m, 6H), 1.74 – 1.64 (m, 1H), 1.63 – 1.50 (m, 1H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 157.0, 154.8, 144.3, 130.3, 130.0, 129.3, 127.3, 121.0, 120.4, 114.4, 111.2, 111.1, 79.1, 67.9, 57.2, 55.2, 46.4, 36.5, 32.7, 31.7, 31.1, 28.7, 26.6, 23.5.

FT-IR (film): 3486, 2920, 2354, 1682, 1046, 964, 744, 700 cm^{-1}.

LC-MS (ESI-MS) *m/z* [M+Na]$^+$ calcd for $C_{27}H_{37}NNaO_4$: 462.3, found: 462.2.

$[\alpha]^{23}_D$ = –30.1 (*c* 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L2**.



2-(3-(2-(3-Methoxyphenethyl)phenoxy)propyl)-1-methylpyrrolidine (78). In the air, $LiAlH_4$ (19.0 mg, 0.50 mmol, 5.0 equiv) was added to a solution of *tert*-butyl 2-(3-(2-(3-methoxyphenethyl)phenoxy)propyl)pyrrolidine-1-carboxylate (43.9 mg, 0.10 mmol, 1.0 equiv) in THF (2.0 mL) at 0 °C, and then the reaction mixture was heated at reflux for 24 h. The reaction was quenched with water (5.0 mL) at 0 °C, and the reaction mixture was then extracted with Et_2O (10 mL x 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the product. Colorless oil.

(*S*,*S*)-**L2**: 35.7 mg, 99% yield; (*R*,*R*)-**L2**: 35.5 mg, 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 2H), 7.15 – 7.09 (m, 1H), 6.90 – 6.81 (m, 3H), 6.78 – 6.72 (m, 2H), 4.06 – 3.95 (m, 2H), 3.79 (s, 3H), 3.14 – 3.04 (m, 1H), 2.99 – 2.83 (m, 4H), 2.32 (s, 3H), 2.22 – 2.05 (m, 2H), 2.05 – 1.64 (m, 6H), 1.59 – 1.38 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 157.0, 144.3, 130.4, 130.0, 129.3, 127.3, 121.0, 120.3, 114.3, 111.13, 111.11, 68.0, 66.2, 57.4, 55.2, 40.5, 36.5, 32.8, 30.8, 30.3, 26.7, 21.9.

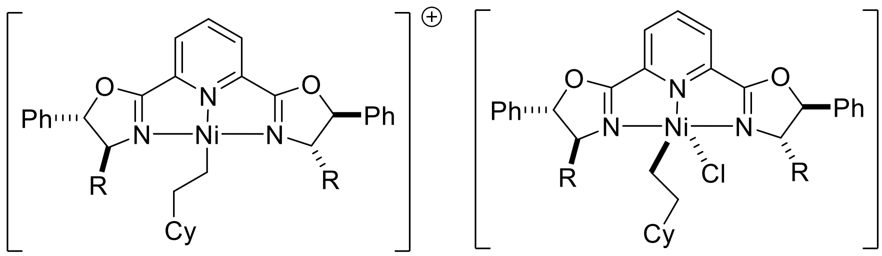
FT-IR (film): 2915, 2353, 1600, 1469, 1247, 1168, 1111, 1047, 874, 752, 695 cm^{-1}.

LC-MS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{32}NO_2$: 354.2, found: 354.2.

$[\alpha]^{23}_D = -32.8$ (*c* 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L2**.

X. Mechanistic Experiments

1. ESI-MS analysis using an alkyl chloride as the electrophile.



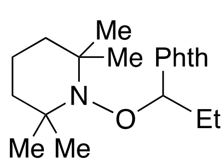
A[1] R = $CH_2OTBDPS$ **A**[2] R = $CH_2OTBDPS$

Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a stir bar was charged with $NiBr_2$·glyme (3.1 mg, 0.010 mmol, 10 mol%) and (*S*,*S*)-**L1** (10.9 mg, 0.012 mmol, 12 mol%). Next, THF (1.0 mL) was added, the vial was capped with a PTFE septum cap, and the mixture was stirred at room temperature for 30 min, at which time it had turned to an orange, homogeneous solution. Then, a solution of 2-(1-chloropropyl)isoindoline-1,3-dione (22.3 mg, 0.10 mmol, 1.0 equiv) in THF (1.0 mL) was added to the reaction mixture. The vial was capped with a PTFE septum cap and taken out of the glovebox. The reaction vial was then placed in an *i*-PrOH cooling bath at 0 °C, and the reaction mixture was stirred at 0 °C for 10 min. Then, **Zn-1** (0.11 mmol, 1.1 equiv) was added dropwise via microsyringe over 3 min, during which the reaction mixture turned dark. The punctures on the septum cap were sealed with grease, and the mixture was stirred at 0 °C for 12 h. Then, an ESI-MS analysis of the reaction was carried out on a Waters LCT Premier XE TOF MS in electrospray ionization (ESI+) mode.

A[1]: HRMS (ESI-MS) *m/z* $[M]^+$ calcd for $C_{65}H_{74}N_3NiO_4Si_2$: 1074.4566, found: 1074.4572.

A[2]: HRMS (ESI-MS) *m/z* $[M]^+$ calcd for $C_{65}H_{74}ClN_3NiO_4Si_2$: 1109.4254, found: 1109.4287.

2. TEMPO trap experiments using an alkyl chloride as the electrophile.



2-(1-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)propyl)isoindoline-1,3-dione. In a nitrogen-filled glovebox, an oven-dried 8 mL vial that contained a stir bar was charged with $NiBr_2$·glyme (6.2 mg, 0.020 mmol, 10 mol%) and (*S*,*S*)-**L1** (21.8 mg, 0.024 mmol, 12 mol%). Next, THF (2.0 mL) was added, the vial was capped with a PTFE septum cap, and the mixture was stirred at room temperature for 30 min, after which time it had turned to an orange, homogeneous solution. Then, a solution of 2-(1-chloropropyl)isoindoline-1,3-dione (44.6 mg, 0.20 mmol, 1.0 equiv) in THF (2.0 mL) was added to the reaction mixture, followed by the addition of TEMPO (31.2 mg, 0.20 mmol, 1.0 equiv). The vial was capped with a PTFE septum cap and taken out of the glovebox. The reaction vial was then placed in an *i*-PrOH cooling bath at 0 °C, and the reaction mixture was stirred at 0 °C for 10 min. Then, **Zn-1** (0.22 mmol, 1.1 equiv) was added dropwise via microsyringe over 3 min, during which the reaction mixture turned dark. The punctures on the septum cap were sealed with grease, and the mixture was stirred at 0 °C for 36 h. The reaction was quenched at 0 °C by the addition of MeOH (0.1 mL). The reaction mixture was passed through a short pad of silica gel, with Et_2O as the eluent. The solvent was removed under reduced pressure, and the residue was purified by chromatography. 5.2 mg (0.015 mmol, 8% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.80 (m, 2H), 7.80 – 7.65 (m, 2H), 5.69 (dd, *J* = 10.1, 5.0 Hz, 1H), 2.58 – 2.38 (m, 1H), 2.30 – 2.08 (m, 1H), 1.56 – 1.39 (m, 3H), 1.38 – 1.22 (m, 6H), 1.18 (s, 3H), 1.03 (s, 3H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 168.6, 134.1, 132.3, 131.7, 123.6, 123.5, 87.5, 61.1, 59.2, 40.26, 40.25, 33.5, 33.3, 23.8, 20.32, 20.26, 17.2, 10.1.

FT-IR (film): 3470, 2934, 2352, 1715, 1456, 1360, 1022, 725 cm^{-1}.

LC-MS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{20}H_{29}N_2O_3$: 345.2, found: 345.2.

3. Time-course experiments with an NHP ester as the coupling partner.

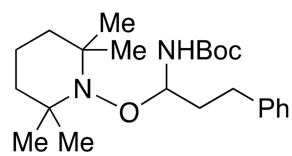
Enantioenriched 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate was synthesized from enantiopure 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoic acid (both enantiomers are commercially available).

Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was equipped with a stir bar and charged with $NiBr_2$·glyme (1.5 mg, 0.0050 mmol, 5.0 mol%), (*S*,*S*)-**L2** (1.8 mg, 0.0060 mmol, 6.0 mol%), and LiCl (8.5 mg, 0.20 mmol, 2.0 equiv). Next, THF (0.4 mL) was added, the vial was capped with a PTFE septum cap, and the mixture was stirred at room temperature for 30 min, during which it became a light-green, homogeneous solution. DMAP (6.1 mg, 0.050 mmol, 0.50 equiv) was added as a stock solution in THF, resulting in a light-blue, homogeneous solution. The solution was then charged with a stock solution of *rac*, (*R*)-, or (*S*)-1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate (42.4 mg, 0.10 mmol, 1.0 equiv) in THF and a stock solution of TMSCl (8.7 mg, 0.080 mmol, 0.80 equiv) in THF, totaling 1.2 mL THF (including 0.4 mL from the catalyst solution). The vial was sealed with a septum cap and wrapped with electrical tape. Next, the vial was removed from the glovebox and cooled to 0 °C using an *i*-PrOH cooling bath. After the white, heterogeneous reaction mixture had stirred at 0 °C for 10 min, **Zn-18** (0.12 mmol, 1.2 equiv) was added dropwise via microsyringe, resulting in a yellow, homogeneous solution. The punctures on the septum cap were sealed with grease, and the mixture was stirred at 0 °C. After 4 h, the reaction was quenched at 0 °C by the addition of MeOH (0.1 mL). The resulting mixture was allowed to warm to room temperature, and then 1-indanone (2.6 mg, 0.020 mmol) was added as an internal standard for LC-MS analysis. The mixture was filtered through a small plug of silica gel, which was flushed with Et_2O (10 mL). A portion of the filtrate (0.1 mL) was diluted with acetone (total volume: 1 mL) and analyzed via LC-MS to determine the amount of product and remaining electrophile. Another portion of the filtrate (0.1 mL) was diluted with acetone (total volume: 1 mL) and analyzed via SFC analysis to determine the ee of the remaining electrophile. The remainder of the filtrate was concentrated under reduced pressure. The pure product was isolated by preparative TLC on silica gel (1:4 EtOAc/hexanes).

SFC analysis of the remaining NHP ester: The ee was determined via SFC on a CHIRALPAK IE column (25% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for (*R*)-enantiomer: 7.6 min, (*S*)-enantiomer: 9.3 min.

HPLC analysis of the product: The ee was determined via HPLC on a CHIRALPAK IC column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 9.1 min (minor), 12.1 min (major).

4. TEMPO trap experiments using an NHP ester as the coupling partner.



***tert*-Butyl (3-phenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propyl)carbamate.** In a nitrogen-filled glovebox, an oven-dried 20 mL vial that contained a cross-type stir bar was charged with $NiBr_2$·glyme (6.2 mg, 0.020 mmol, 5.0 mol%), (*S*,*S*)-**L2** (7.1 mg, 0.024 mmol, 6.0 mol%), and LiCl (33.9 mg, 0.80 mmol, 2.0 equiv). Next, THF (1.6 mL) was added, the vial was capped with a PTFE septum cap, and the mixture was stirred at room temperature for 30 min, during which it became a light-green, homogeneous solution. Next, a solution of 1,3-dioxoisoindolin-2-yl 2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate (170 mg, 0.40 mmol, 1.0 equiv) and DMAP (24.4 mg, 0.20 mmol, 0.50 equiv) in THF (3.2 mL) was added to the reaction mixture, followed by the addition of TMSCl (41μL, 0.32 mmol, 0.80 equiv) via microsyringe. Next, TEMPO (62.5 mg, 0.40 mmol, 1.0 equiv) was added. The vial was sealed with a septum cap and wrapped with electrical tape, and it was then removed from the glovebox and cooled to 0 °C using an *i*-PrOH cooling bath. After the red, slightly opaque mixture had stirred at 0 °C for 10 min, **Zn-18** (0.48 mmol, 1.2 equiv) was added dropwise via microsyringe over 5 min, resulting in a homogeneous, dark red solution. The punctures on the septum cap were sealed with grease, and the mixture was stirred at 0 °C for 18 h. Next, the reaction was quenched at 0 °C by the addition of MeOH (0.2 mL). The resulting mixture was passed through a short pad of silica gel, with Et_2O as the eluent. A small aliquot was taken for HRMS analysis. Attempts to isolate the TEMPO adduct by chromatography were unsuccessful.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{39}N_2O_3$: 391.2955, found: 391.3006.

XI. Assignments of Absolute Configuration

The configuration of the coupling product illustrated in Fig. 2B.1, **6**, using (*R*,*R*)-**L1**, was determined via X-ray crystallography.

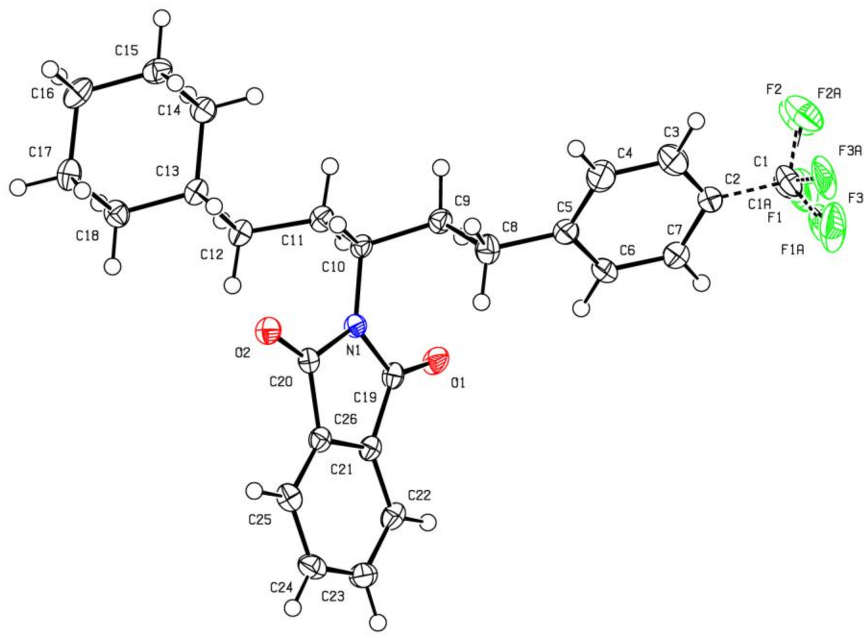
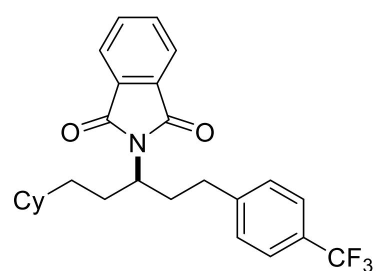


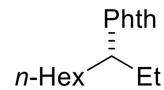
Figure S-1. Thermal ellipsoid plot at the 50% probability level.



(*R*)-2-(1-Cyclohexyl-5-(4-(trifluoromethyl)phenyl)pentan-3-yl)isoindoline-1,3-dione (6). X-ray quality crystals were obtained by slow evaporation of a saturated solution in EtOAc/hexanes of a sample synthesized using (*R*,*R*)-**L1**. A crystal of $C_{26}H_{28}F_3NO_2$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker APEX-II CCD diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[8] the structure was solved with the XT[9] structure solution program using direct methods and refined with the ShelXL[10] refinement package using least squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S-5. Crystal data for $C_{26}H_{28}F_3NO_2$.

Identification code	V20056	
Chemical formula	$C_{26}H_{28}F_3NO_2$	
Formula weight	443.49 g/mol	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal size	0.058 x 0.061 x 0.261 mm	
Crystal habit	clear colourless block	
Crystal system	orthorhombic	
Space group	$P\ 2_1\ 2_1\ 2_1$	
Unit cell dimensions	a = 5.3650(7) Å	α = 90°
	b = 10.7237(14) Å	β = 90°
	c = 38.480(5) Å	γ = 90°
Volume	2213.9(5) $Å^3$	
Z	4	
Density (calculated)	1.331 g/cm^3	
Absorption coefficient	0.837 mm^{-1}	
F(000)	936	
Theta range for data collection	4.28 to 69.64°	
Index ranges	-6<=h<=6, -12<=k<=12, -42<=l<=46	
Reflections collected	16610	
Independent reflections	3988 [R(int) = 0.0568]	
Coverage of independent reflections	97.8%	
Absorption correction	Multi-Scan	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3988 / 196 / 320	
Goodness-of-fit on F^2	1.073	
Final R indices	3783 data; $I>2\sigma(I)$	
	all data	R1 = 0.0462, wR2 = 0.0965
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0252P)^2+1.2048P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.03(9)	
Largest diff. peak and hole	0.213 and -0.258 eÅ^{-3}	
R.M.S. deviation from mean	0.042 eÅ^{-3}	



(*R*)-2-(Nonan-3-yl)isoindoline-1,3-dione (17). The absolute configuration of this compound has been established.[11] The coupling product obtained with (*S*,*S*)-**L1** has the (*R*)-configuration, by comparison with the sign of the published optical rotation.

Optical rotation: $[\alpha]^{22}_{D} = -6.1$ (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L1**.

Lit.: $[\alpha]^{26}_{D} = -17.2$ (*c* 1.0, $CHCl_3$); 99% ee for (*R*)-configuration.

The configuration of the coupling product illustrated in Fig. 5A, **42**, using (*S*,*S*)-**L2**, was determined via X-ray crystallography.

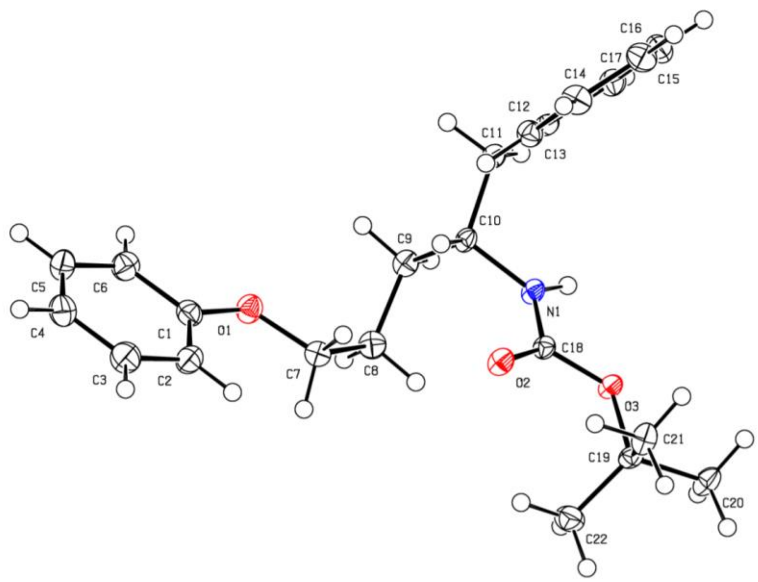
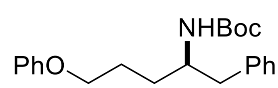


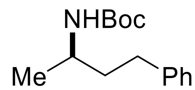
Figure S-2. Thermal ellipsoid plot at the 50% probability level.



***tert*-Butyl (*R*)-(5-phenoxy-1-phenylpentan-2-yl)carbamate (42).** X-ray quality crystals were obtained by slow evaporation of a saturated solution in hexane/pentane of a sample synthesized using (*S*,*S*)-**L2**. A crystal of $C_{22}H_{29}NO_3$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker APEX-II CCD diffractometer with filtered Cu-K*α* radiation at a temperature of 100 K. Using Olex2,[8] the structure was solved with the XT[9] structure solution program using direct methods and refined with the ShelXL[10] refinement package using least squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S-76. Crystal data for $C_{22}H_{29}NO_3$.

Identification code	V20066	
Chemical formula	$C_{22}H_{29}NO_3$	
Formula weight	355.46 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.053 x 0.140 x 0.246 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 10.191(2) Å	α = 90°
	b = 9.3953(19) Å	β = 115.106(8)°
	c = 11.509(3) Å	γ = 90°
Volume	997.8(4) $Å^3$	
Z	2	
Density (calculated)	1.183 g/cm^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	384	
Theta range for data collection	2.92 to 28.29°	
Index ranges	-13<=h<=13, -12<=k<=12, -15<=l<=15	
Reflections collected	44841	
Independent reflections	4963 [R(int) = 0.0712]	
Coverage of independent reflections	99.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9960 and 0.9810	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4963 / 1 / 238	
Goodness-of-fit on F^2	1.082	
Final R indices	4598 data; I>2σ(I)	R1 = 0.0359, wR2 = 0.0789
	all data	R1 = 0.0411, wR2 = 0.0808
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0340P)^2+0.1542P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.1(3)	
Largest diff. peak and hole	0.192 and -0.202 e$Å^{-3}$	
R.M.S. deviation from mean	0.036 e$Å^{-3}$	



***tert*-Butyl (*R*)-(4-phenylbutan-2-yl)carbamate (51)**. The absolute configuration of this compound has been established.[5] The coupling product obtained with (*S*,*S*)-**L2** has the (*R*)-configuration, by comparison with published optical rotation.

Optical rotation: $[\alpha]^{23}_{D}$ = +10.6 (c 1.0, $CHCl_3$); 81% ee, from (*S*,*S*)-**L2**.

Lit.: $[\alpha]^{25}_{D}$ = +13.9 (c 0.9, $CHCl_3$); 96% ee for (*R*)-configuration.

XII. References

(1) Eno, M. S.; Lu, A.; Morken, J. P. Nickel-Catalyzed Asymmetric Kumada Cross-Coupling of Symmetric Cyclic Sulfates. *J. Am. Chem. Soc.* **2016**, *138*, 7824–7827.

(2) Kim, H.; Nguyen, Y.; Yen, C. P.-H.; Chagal, L.; Lough, A. J.; Kim, B. M.; Chin, J. Stereospecific Synthesis of C_2 Symmetric Diamines from the Mother Diamine by Resonance-Assisted Hydrogen-Bond Directed Diaza-Cope Rearrangement. *J. Am. Chem. Soc.* **2008**, *130*, 12184–12191.

(3) Koley, D.; Krishna, Y.; Srinivas, K.; Khan, A. A.; Kant, R. Organocatalytic Asymmetric Mannich Cyclization of Hydroxylactams with Acetals: Total Syntheses of (−)-Epilupinine, (−)-Tashiromine, and (−)-Trachelanthamidine**.** *Angew. Chem. Int. Ed.* **2014**, *53*, 13196–13200.

(4) Krasovskiy, A.; Knochel, P. Convenient Titration Method for Organometallic Zinc, Magnesium, and Lanthanide Reagents. *Synthesis* **2006**, 890–891.

(5) Nechab, M.; El Blidi, L.; Vanthuyne, N.; Gastaldi, S.; Bertrand, M. P.; Gil, G. *N*-Acyl glycinates as acyl donors in serine protease-catalyzed kinetic resolution of amines. Improvement of selectivity and reaction rate. *Org. Biomol. Chem.* **2008**, *6*, 3917–3920.

(6) Spyropoulos, C.; Kokotos, C. G. One-Pot Synthesis of Ureas from Boc-Protected Amines. *J. Org. Chem.* **2014**, *79*, 4477–4483.

(7) Nasopoulou, M.; Georgiadis, D.; Matziari, M.; Dive, V.; Yiotakis, A. A Versatile Annulation Protocol toward Novel Constrained Phosphinic Peptidomimetics. *J. Org. Chem.* **2007**, *72*, 7222–7228.

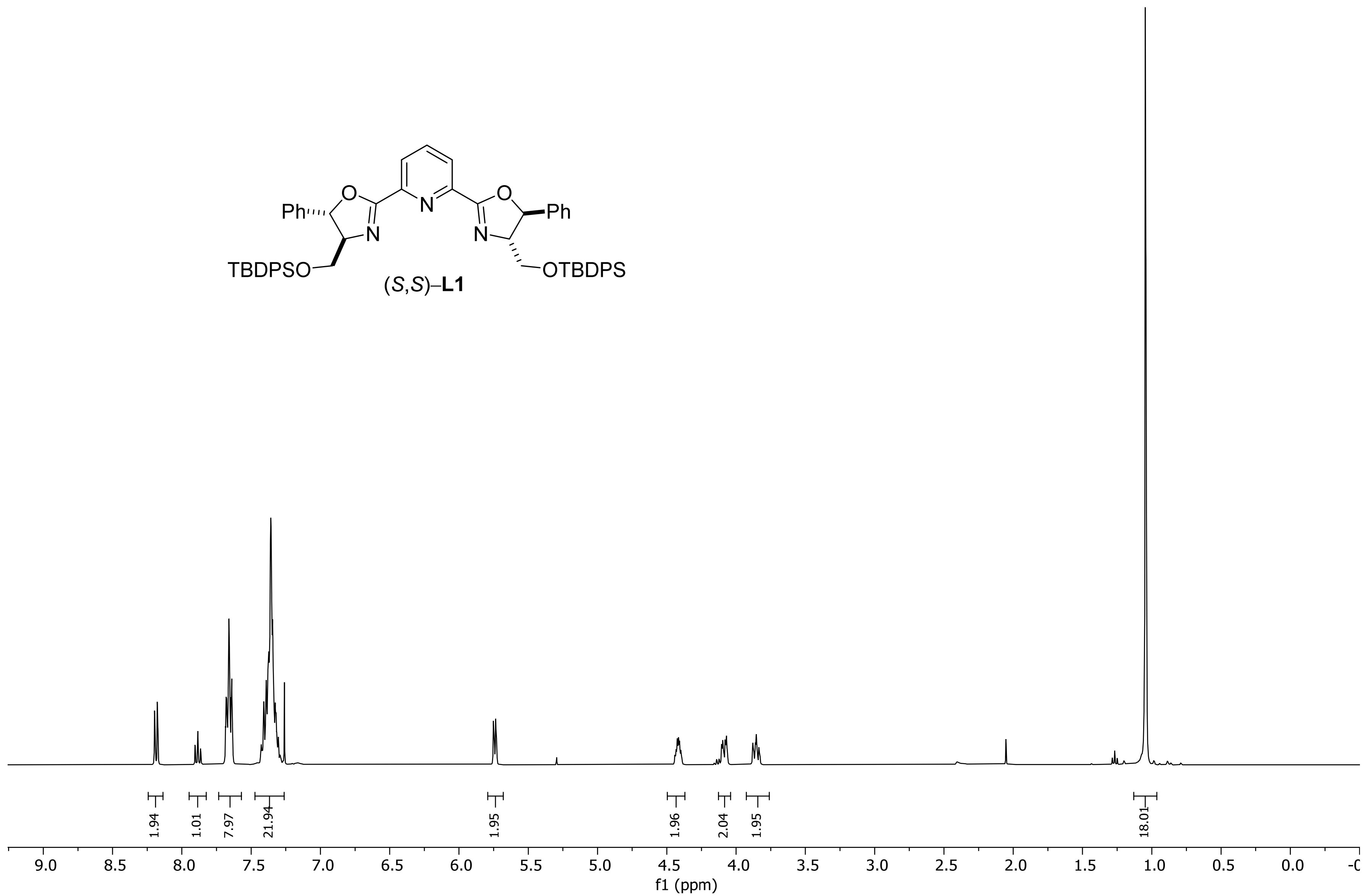
(8) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341.

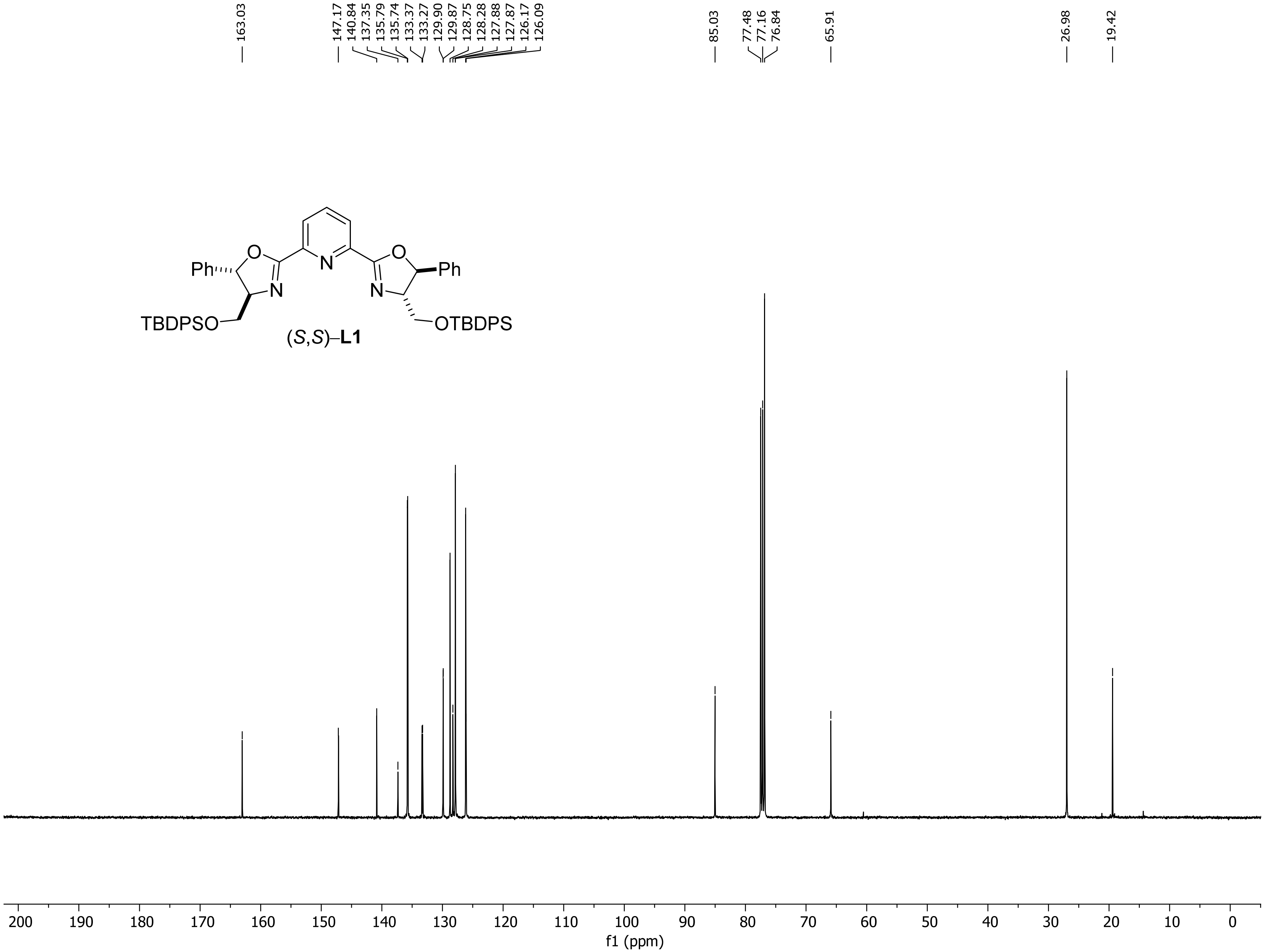
(9) Sheldrick, G. M. *SHELXT* - Integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015**, *71*, 3–8.

(10) Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr. C* **2015**, *71*, 3–8.

(11) Oodera, J.; Sato, T. Preparation of Optically Active Organic Compound by SubstitutionReaction with Configurational Inversion. Jpn. Patent 05294850, 1993.

XIII. NMR Spectra and Determination of Stereoselectivity

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140.84
137.35
135.79
135.74
133.37
133.27
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129.87
128.75
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127.88
127.87
126.17
126.09
85.03
77.48
77.16
76.84
65.91
26.98
19.42
Ph
O
N
TBDPSO
OTBDPS
(S,S)–L1
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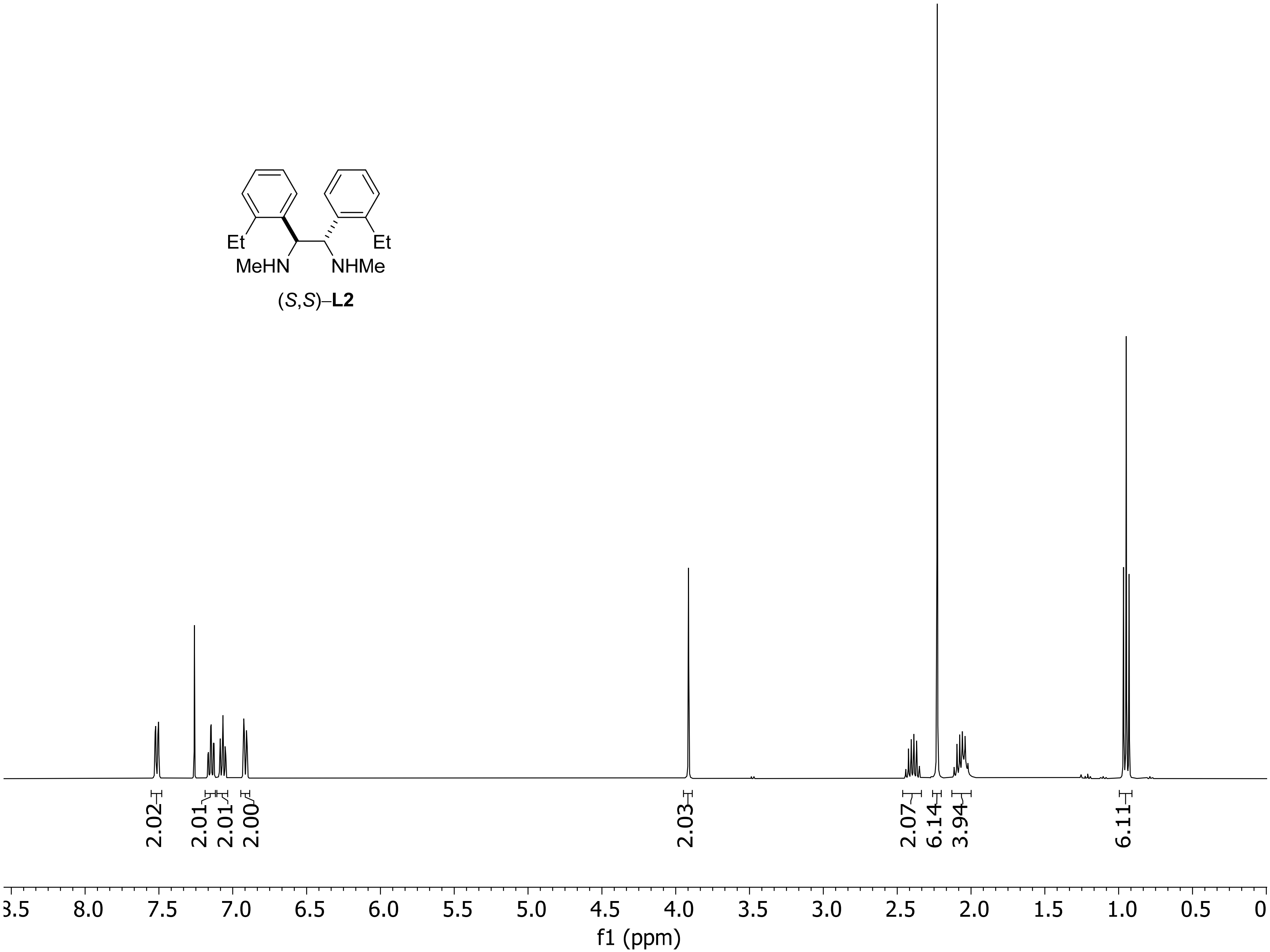
f1 (ppm)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MeHN
NHMe
Et
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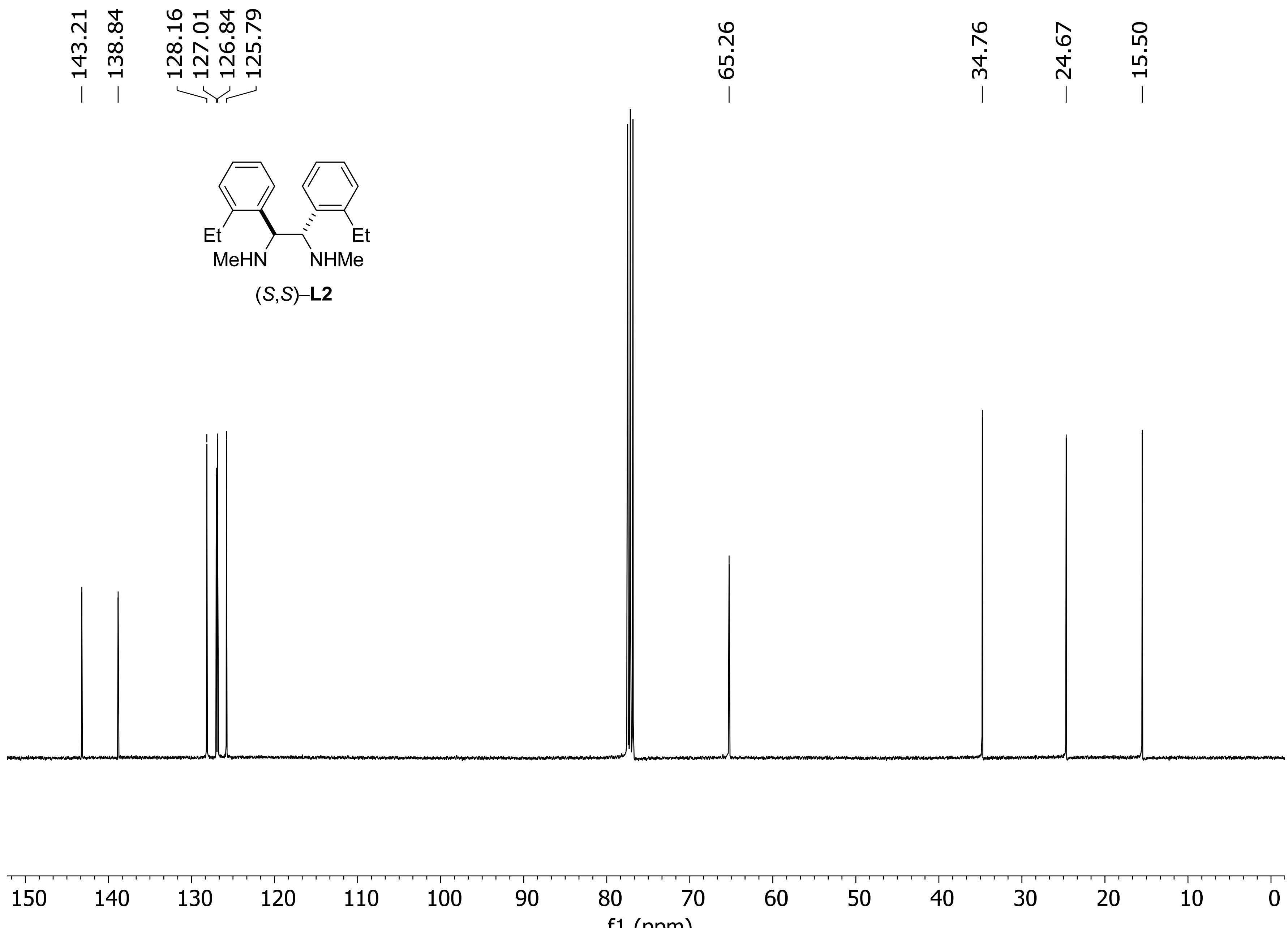
2.01
2.01
2.00
2.03
2.07
6.14
3.94
6.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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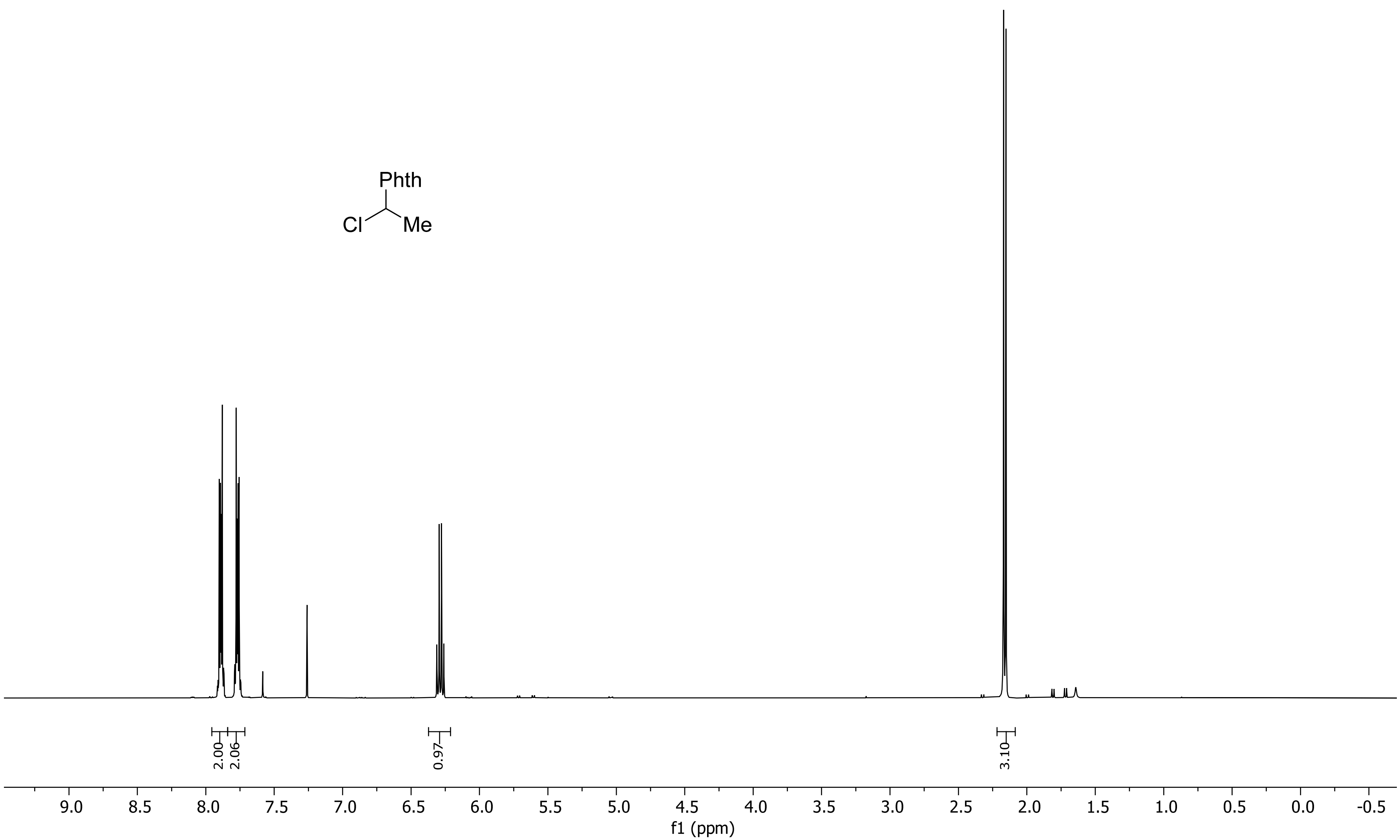
138.84
128.16
127.01
126.84
125.79
65.26
34.76
24.67
15.50
Et
MeHN
NHMe
Et
(S,S)–L2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.5
8.0
7.5
7.0
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6.0
5.5
5.0
4.5
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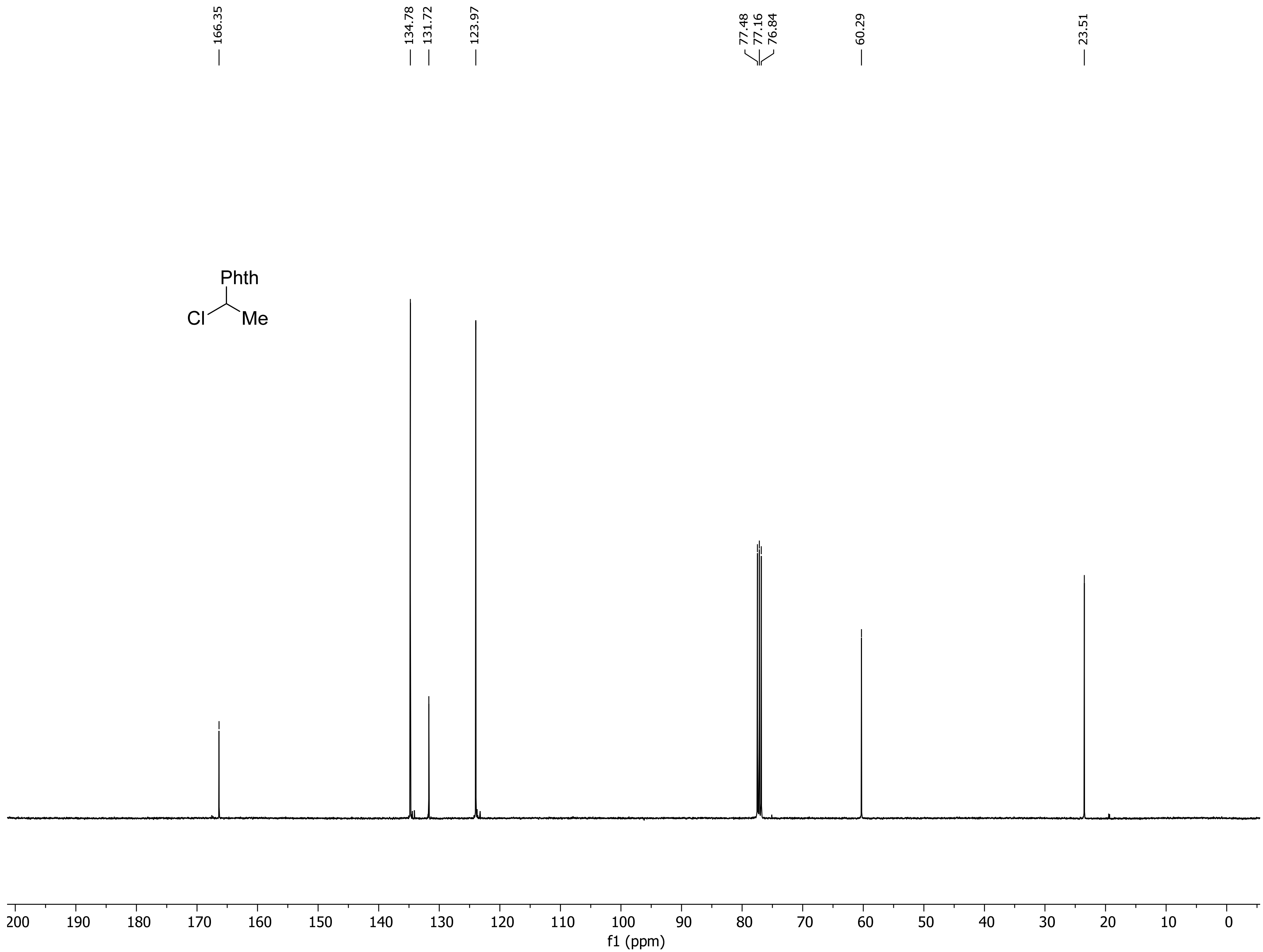
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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134.78
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60.29
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Phth
Cl
Me
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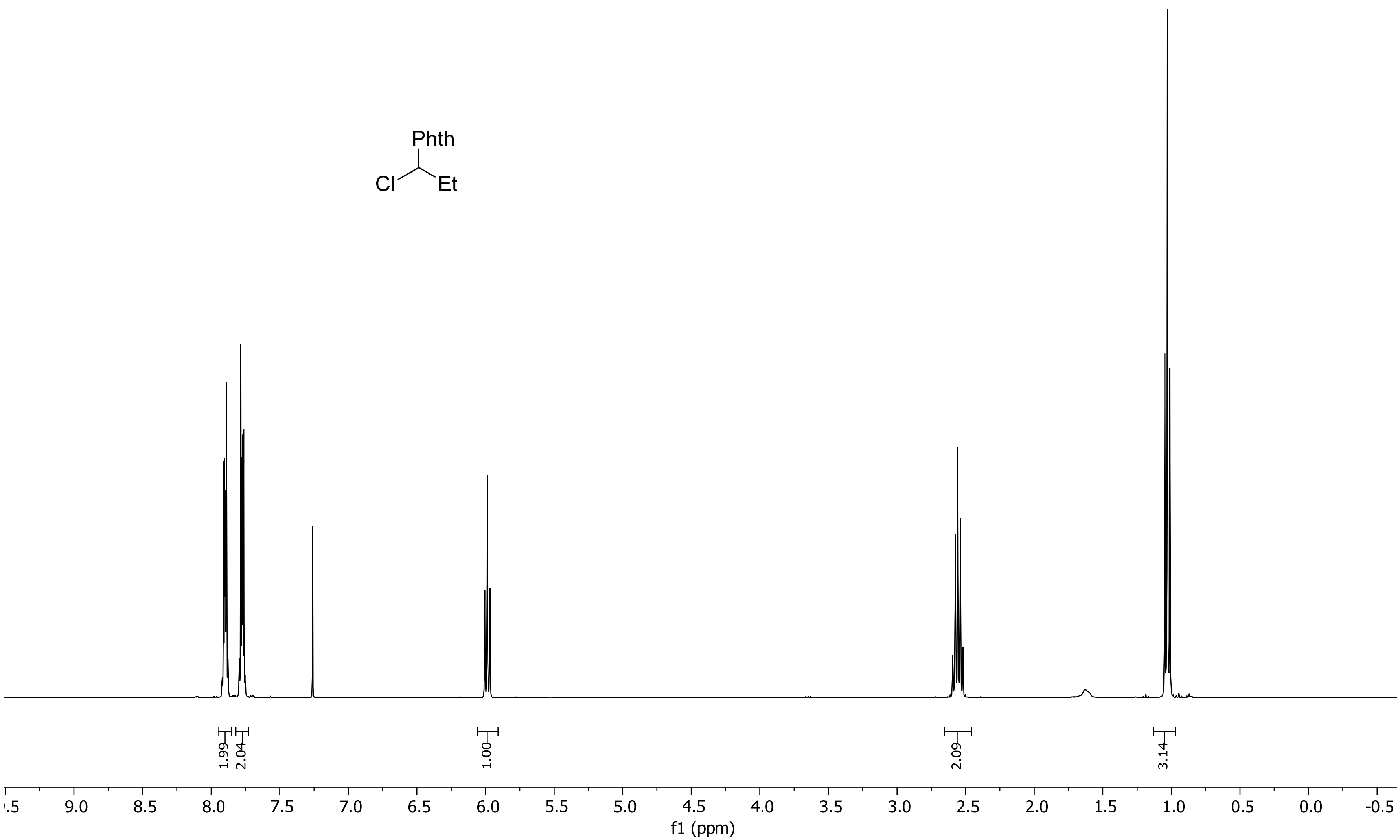
f1 (ppm)



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Et
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3.14
.5
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8.5
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
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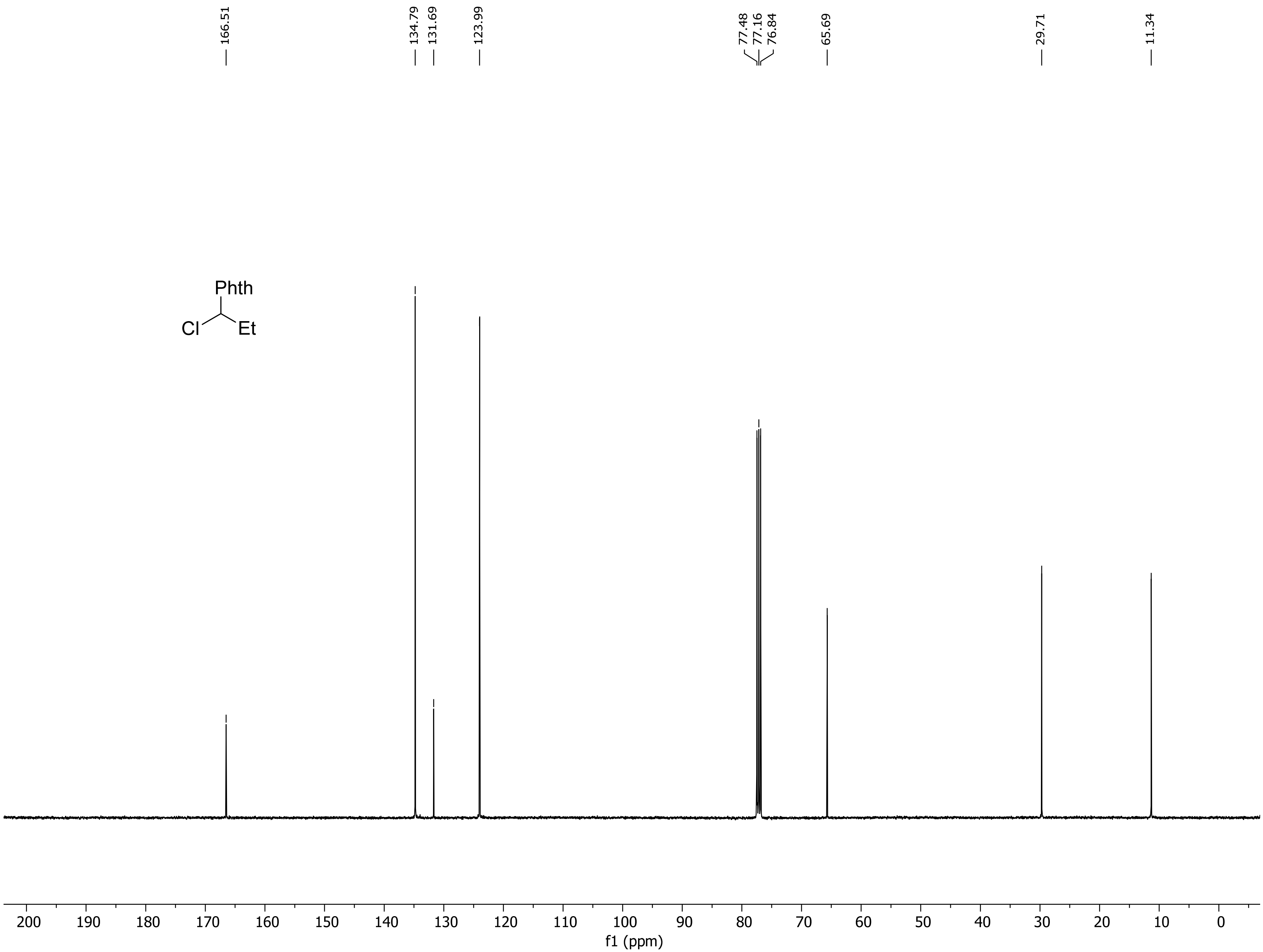
0.5
0.0
-0.5
f1 (ppm)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Et
200
190
180
170
160
150
140
130
120
110
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90
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70
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40
30
20
10
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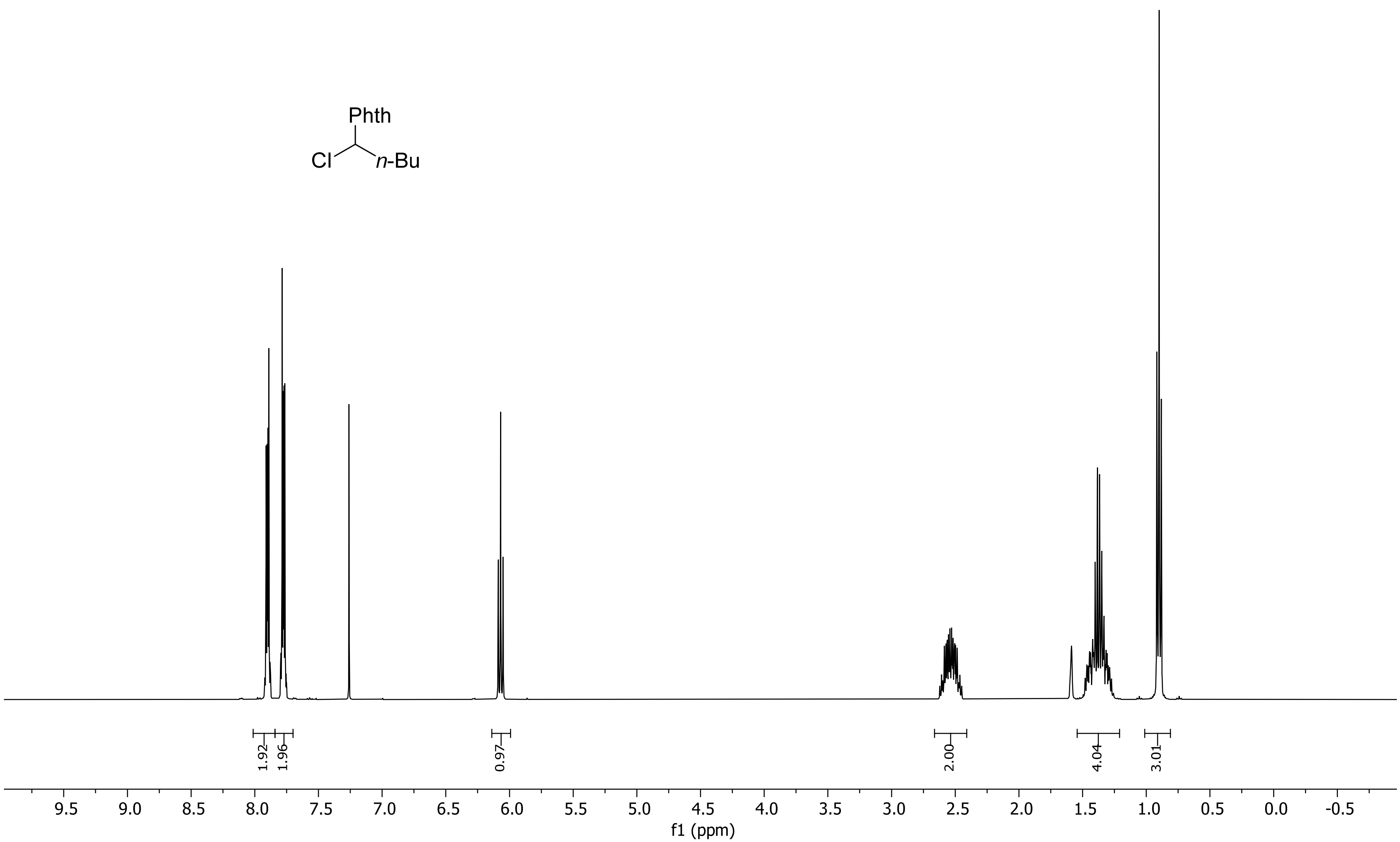
f1 (ppm)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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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0.5
0.0
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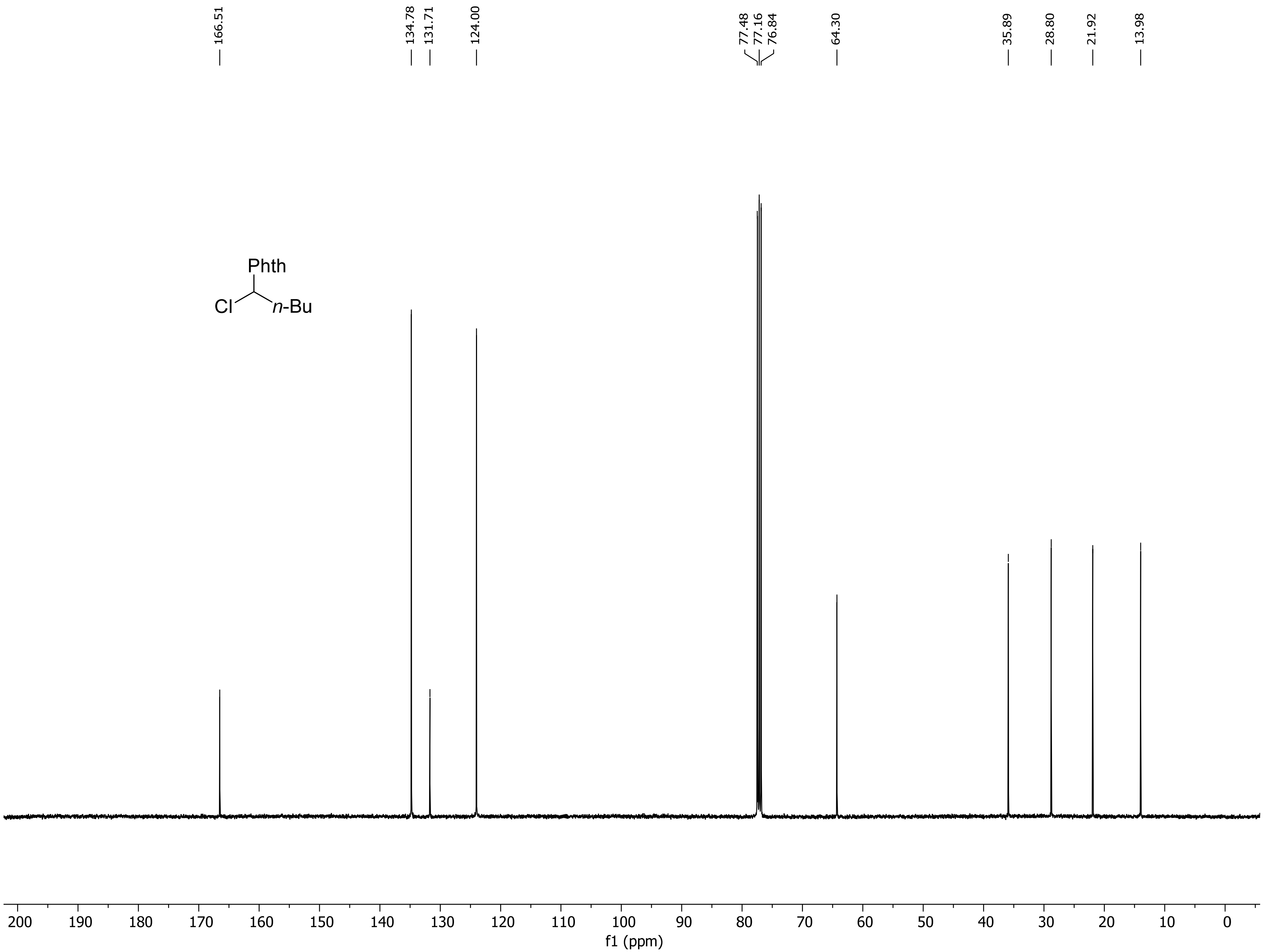
f1 (ppm)



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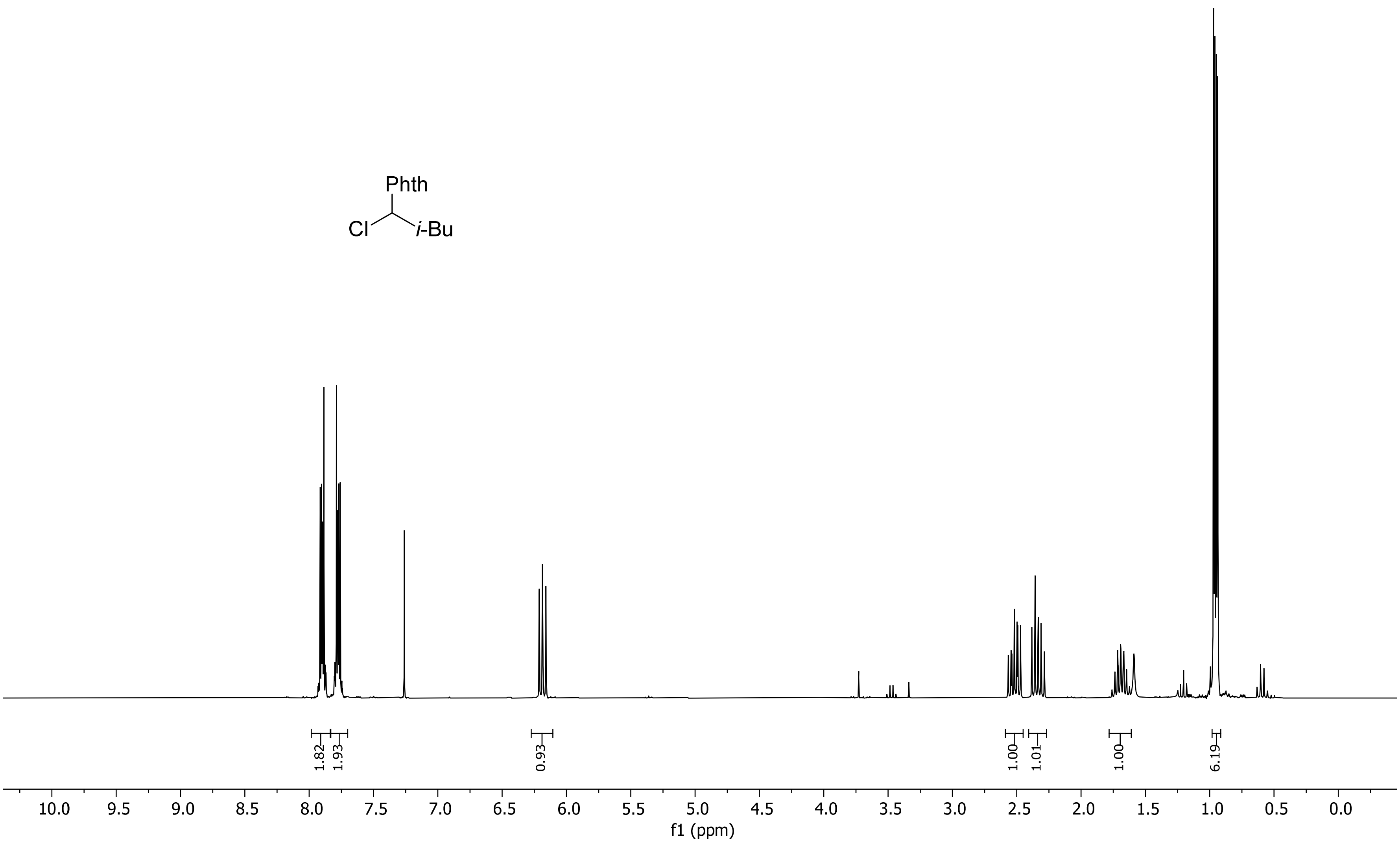
134.78
131.71
124.00
77.48
77.16
76.84
64.30
35.89
28.80
21.92
13.98
Phth
Cl
n-Bu
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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1.00
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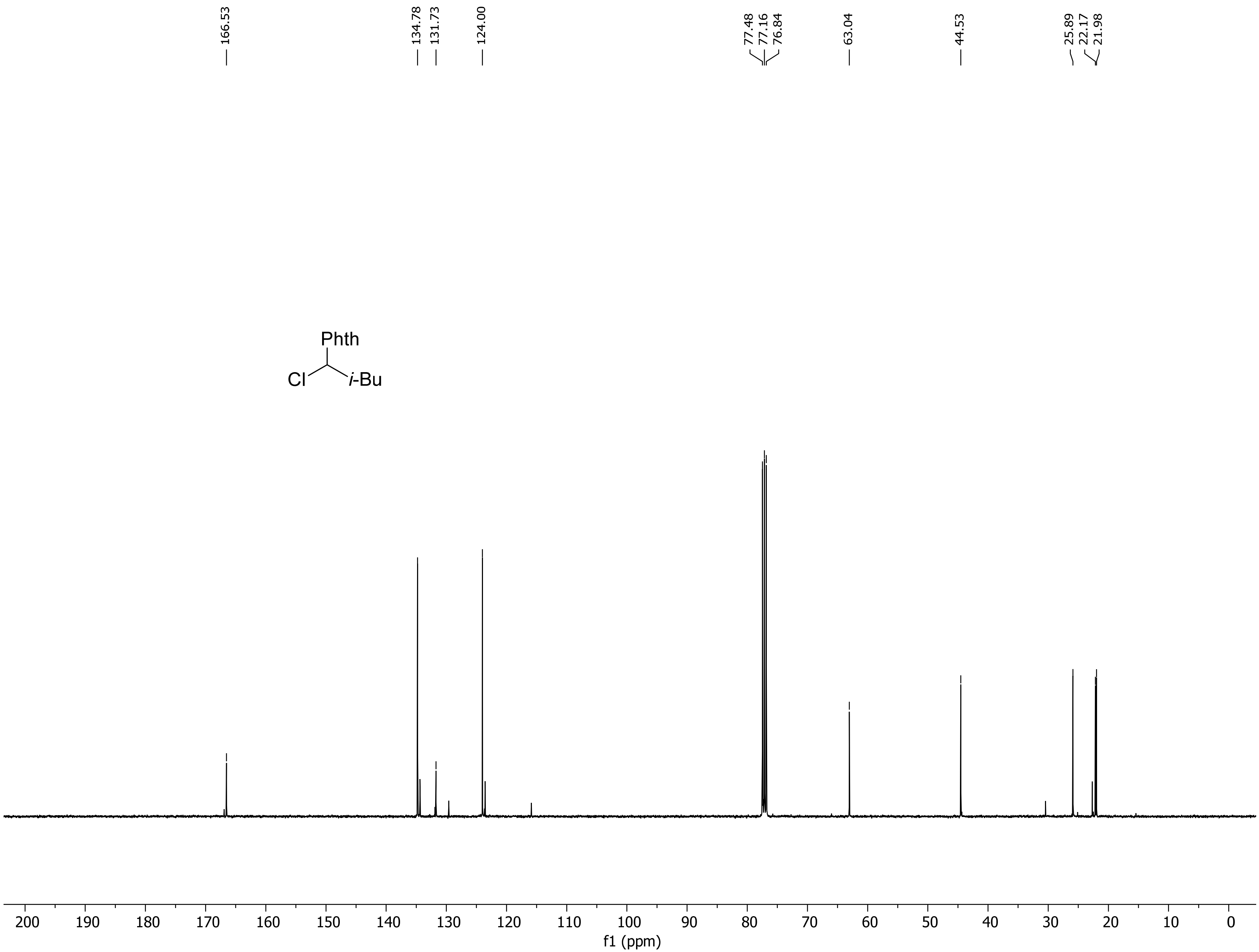
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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Cl
i-Bu
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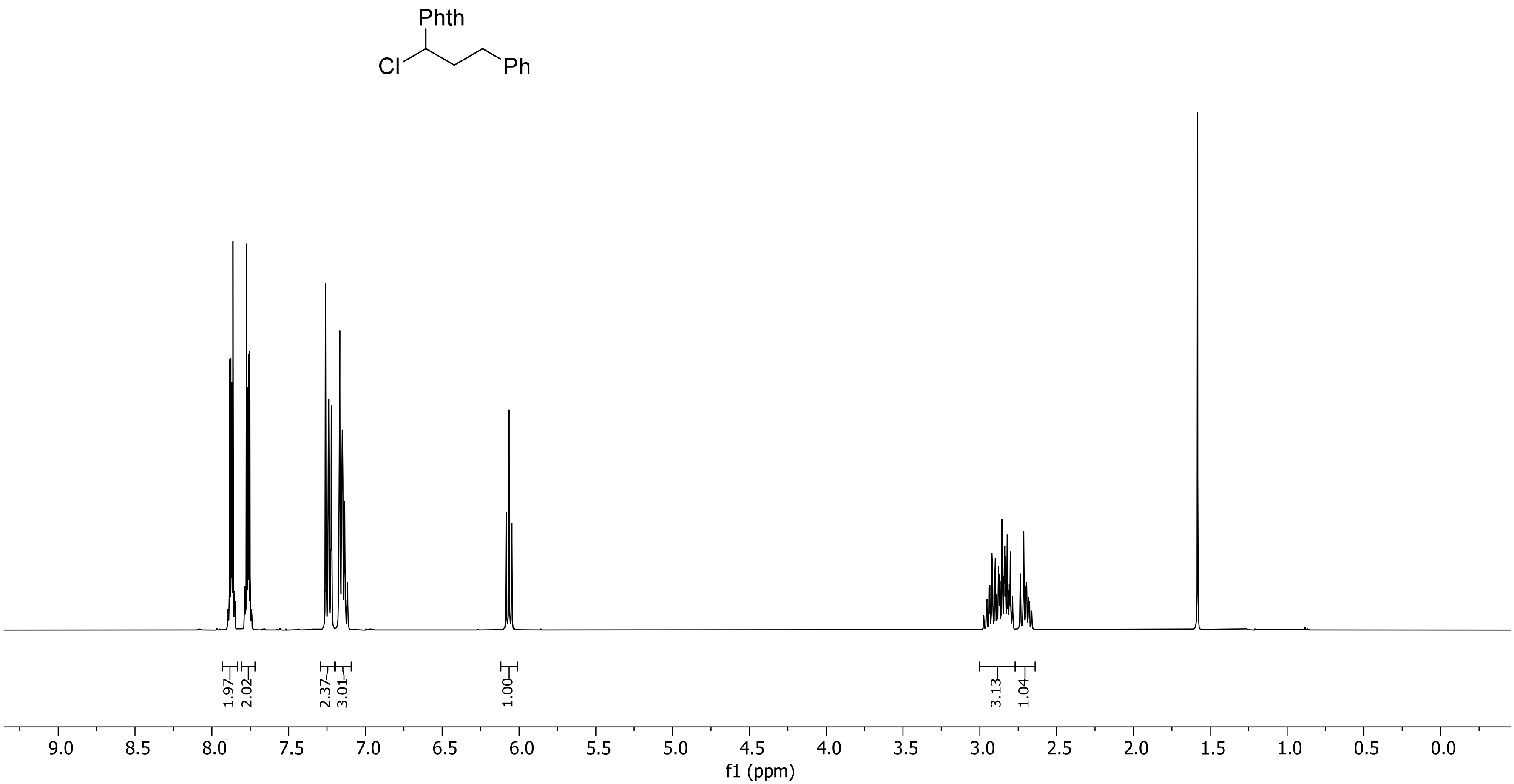
f1 (ppm)


Phth
Cl
Ph
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7.0
6.5
6.0
5.5
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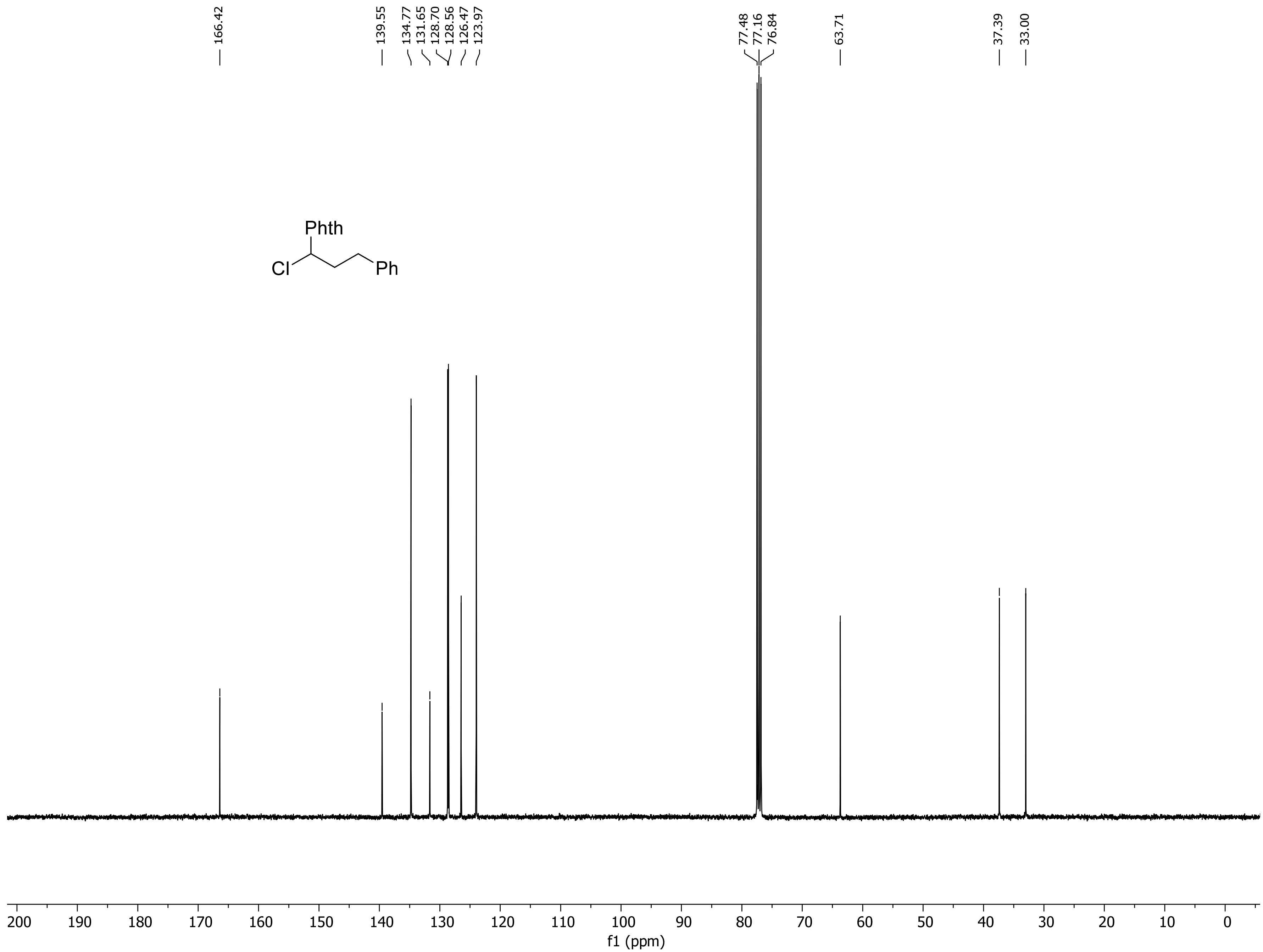
f1 (ppm)



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128.70
128.56
126.47
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77.16
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33.00
Phth
Cl
Ph
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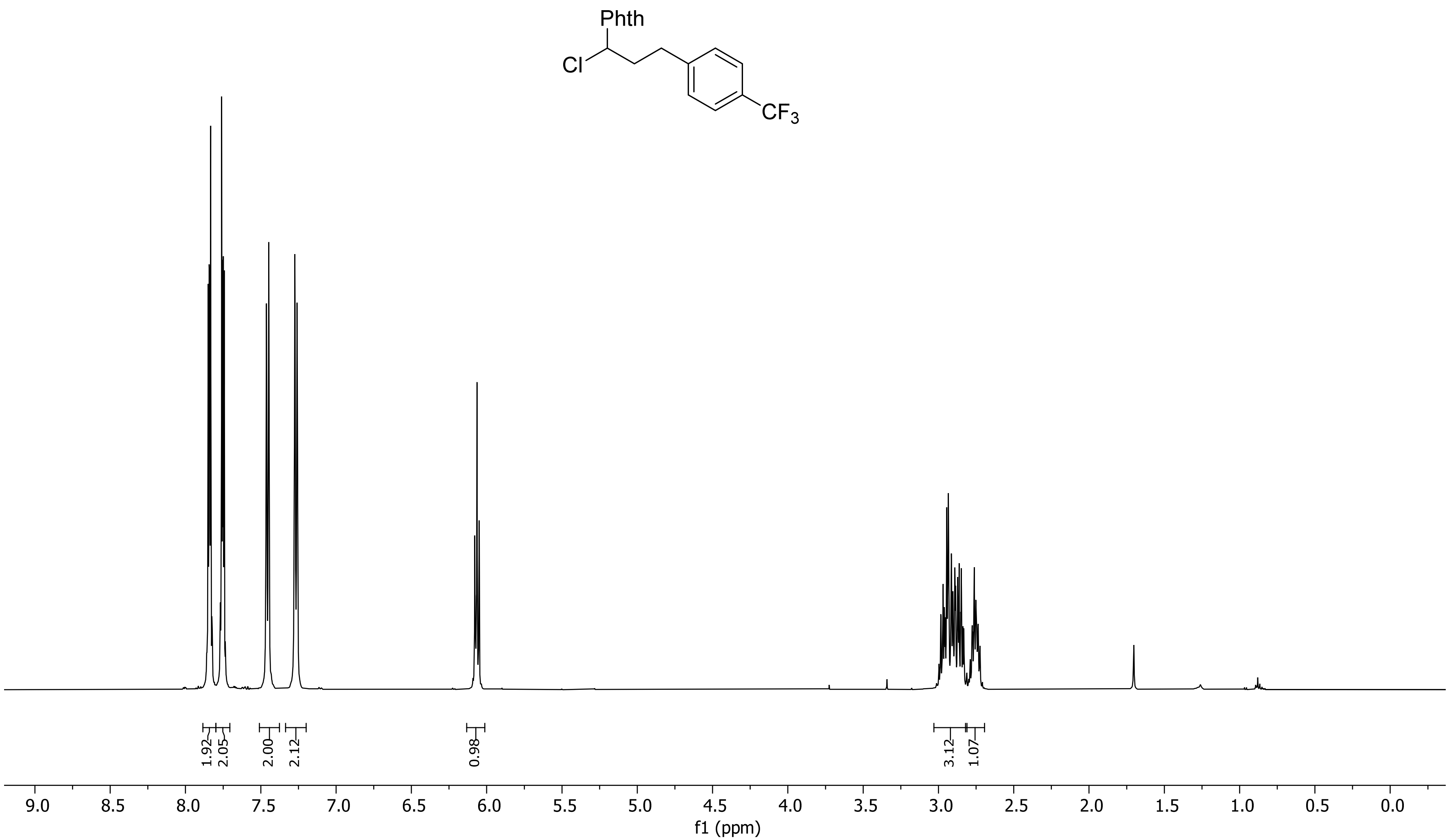
f1 (ppm)



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7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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2.5
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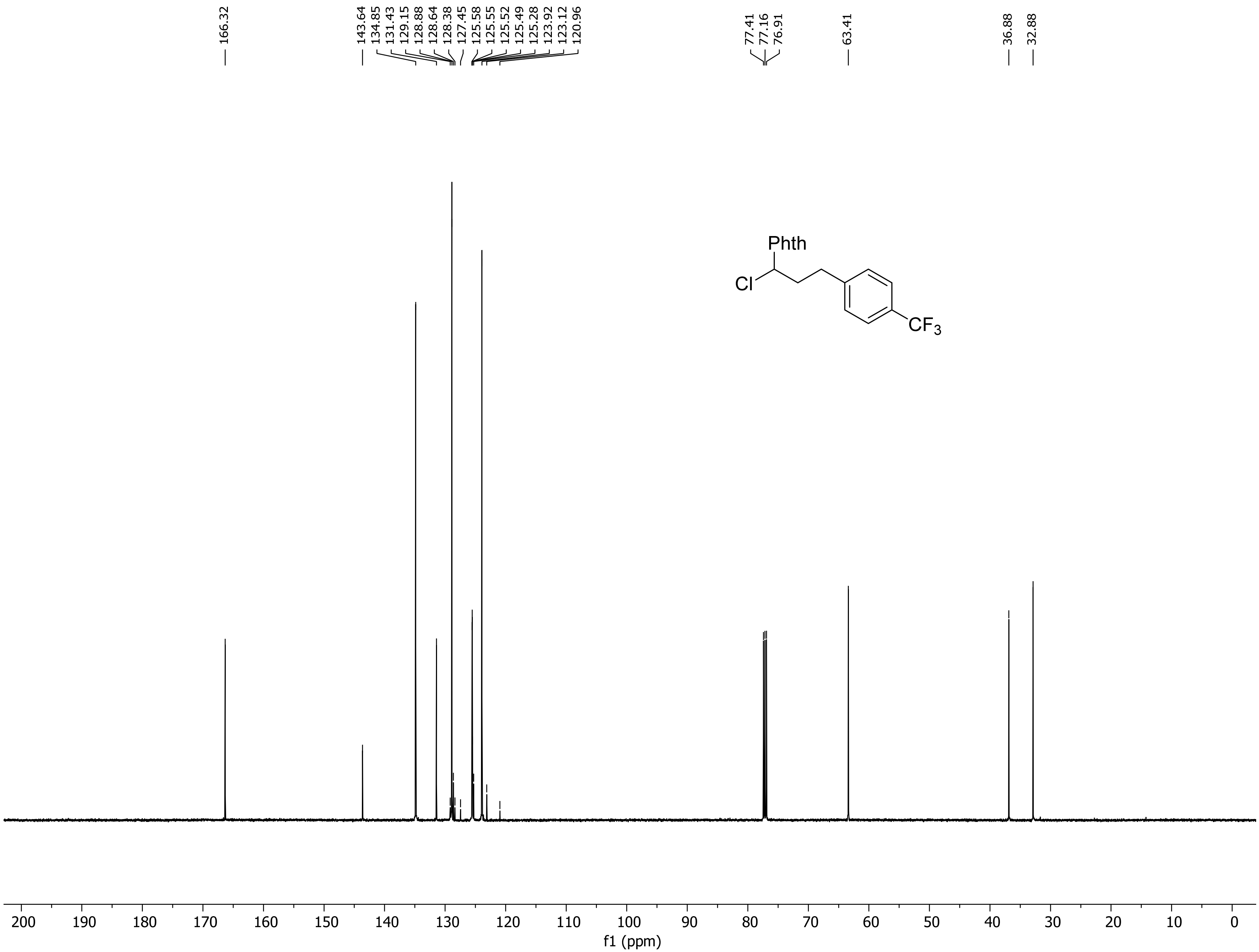
1.0
0.5
0.0
f1 (ppm)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123.12
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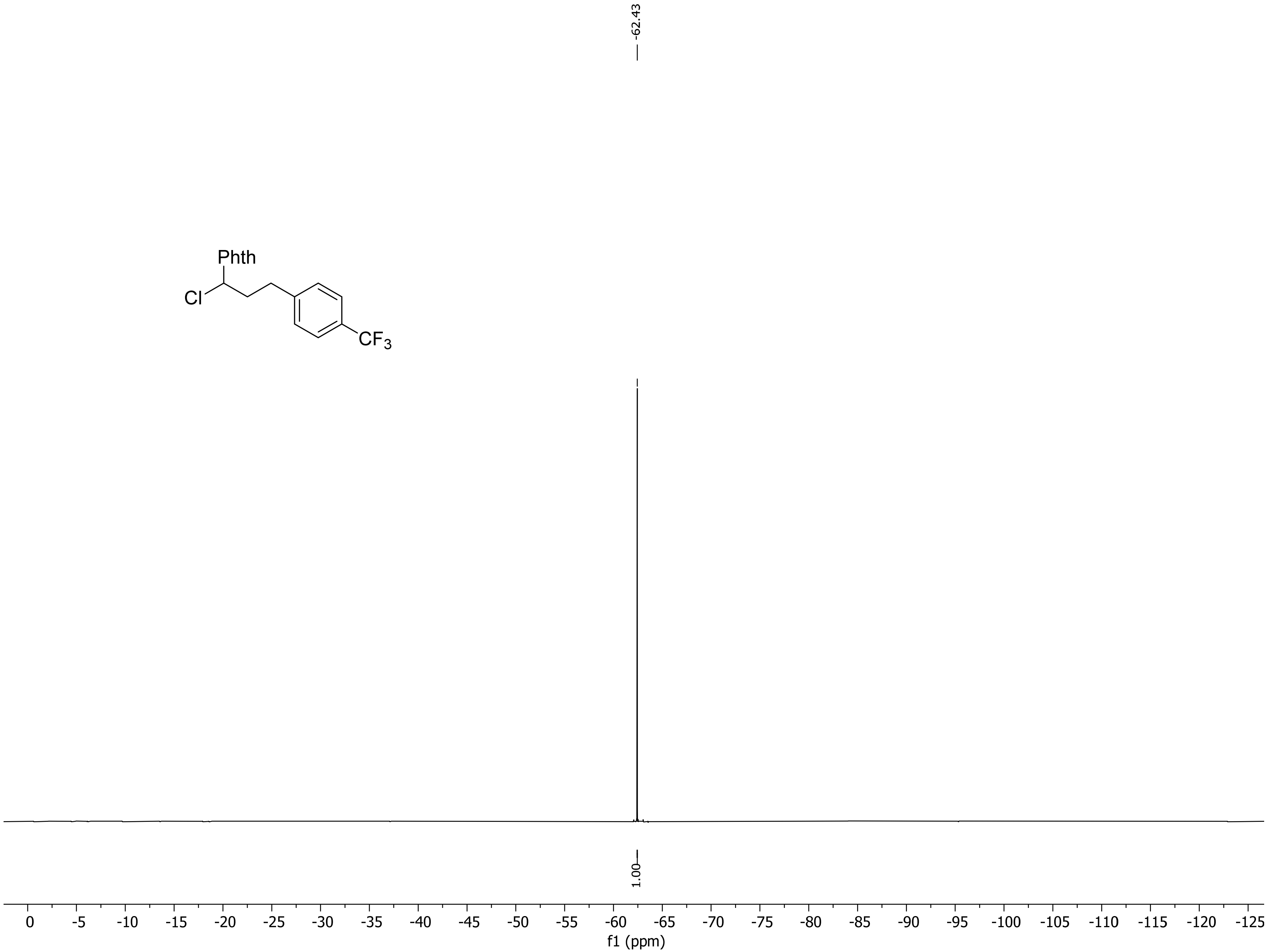
77.41
77.16
76.91
63.41
36.88
32.88
Phth
Cl
CF3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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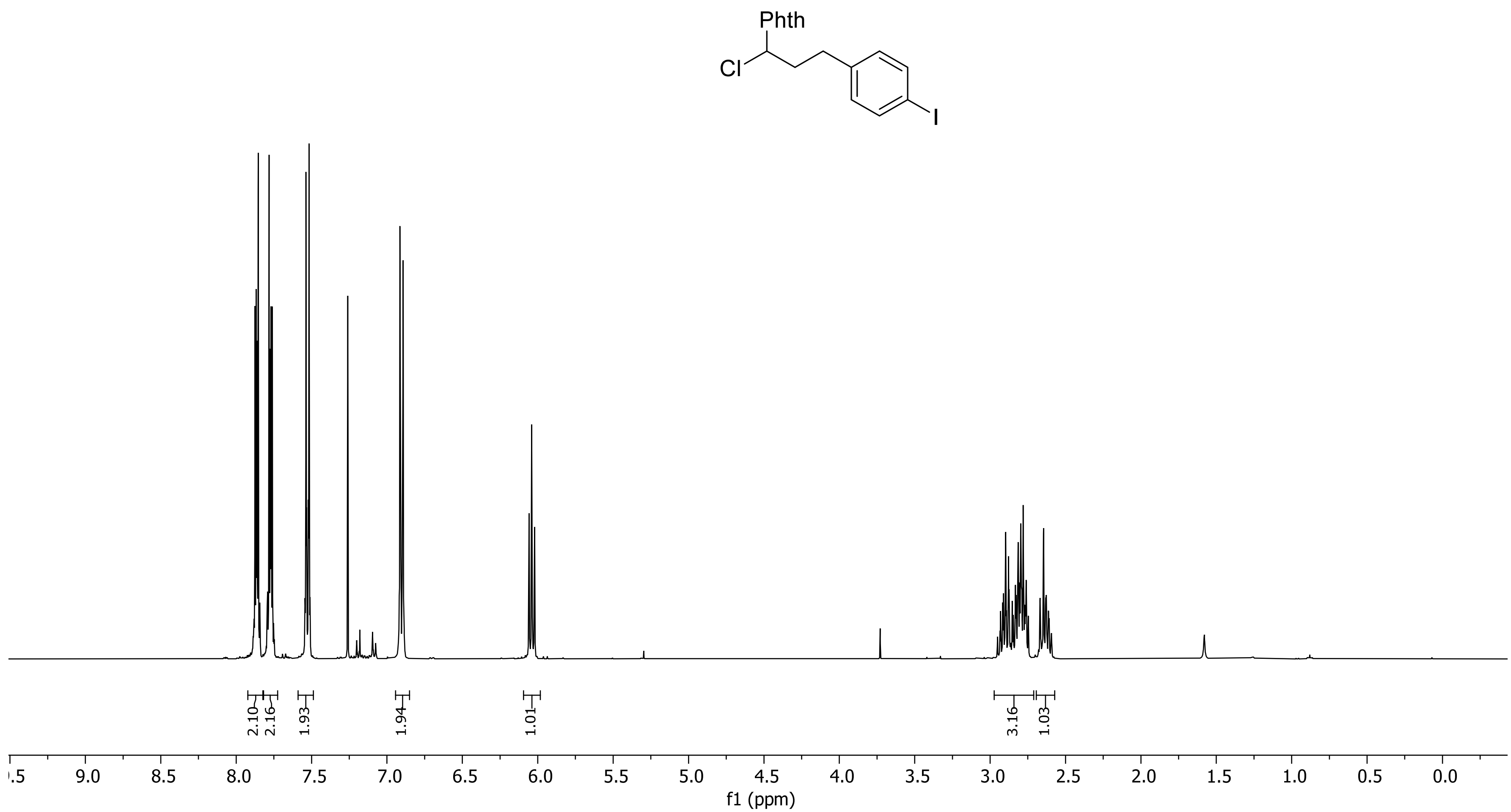
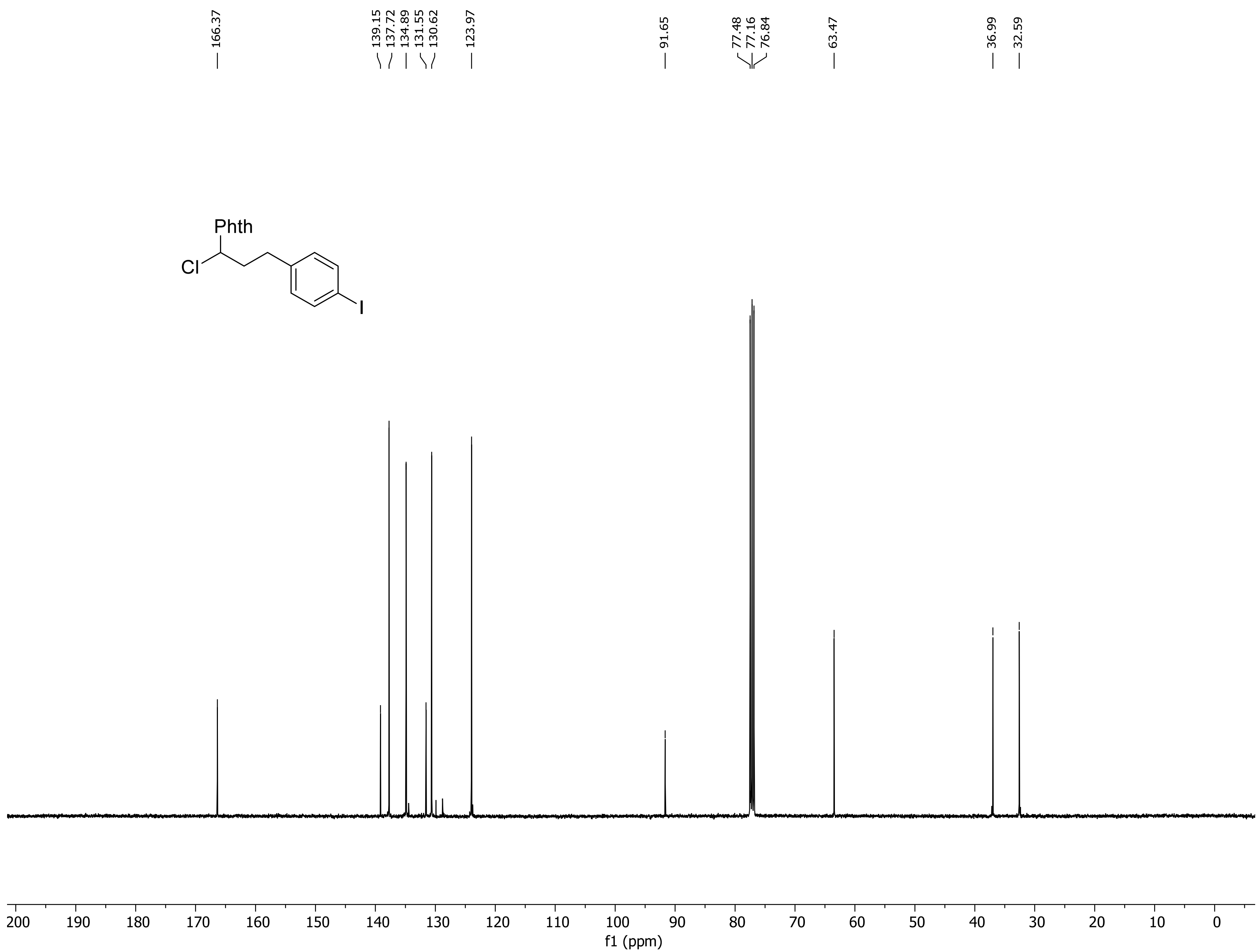
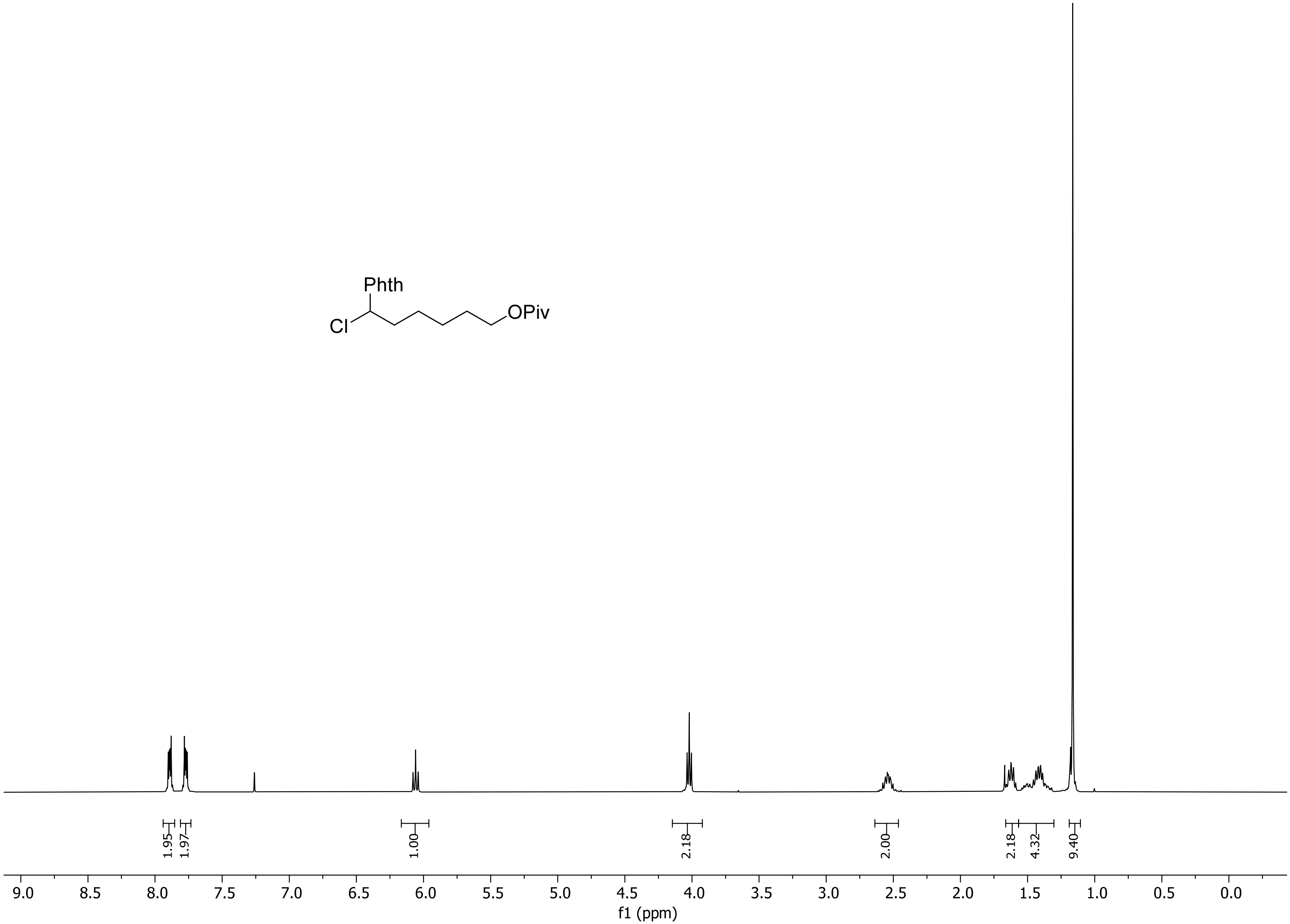
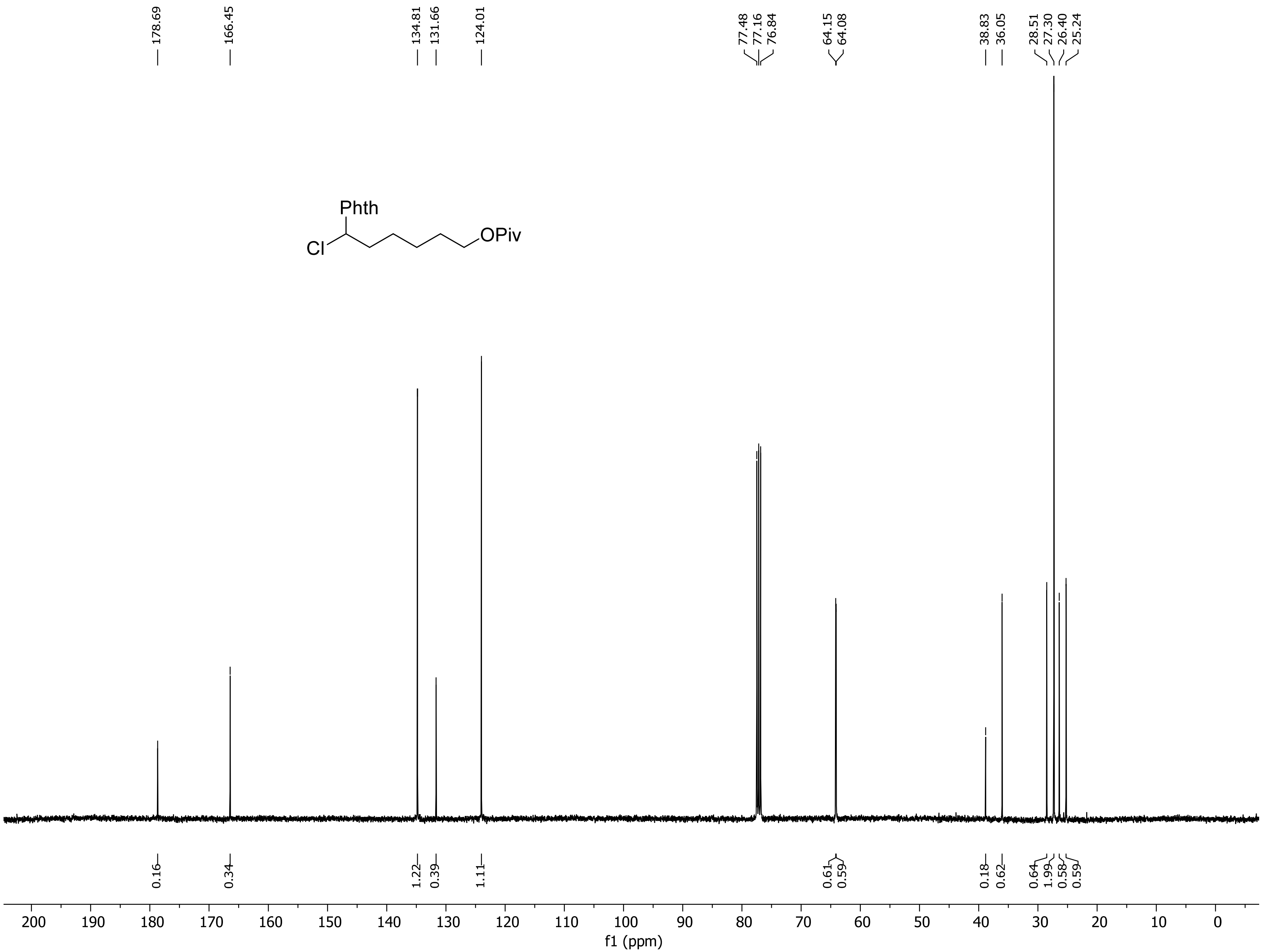
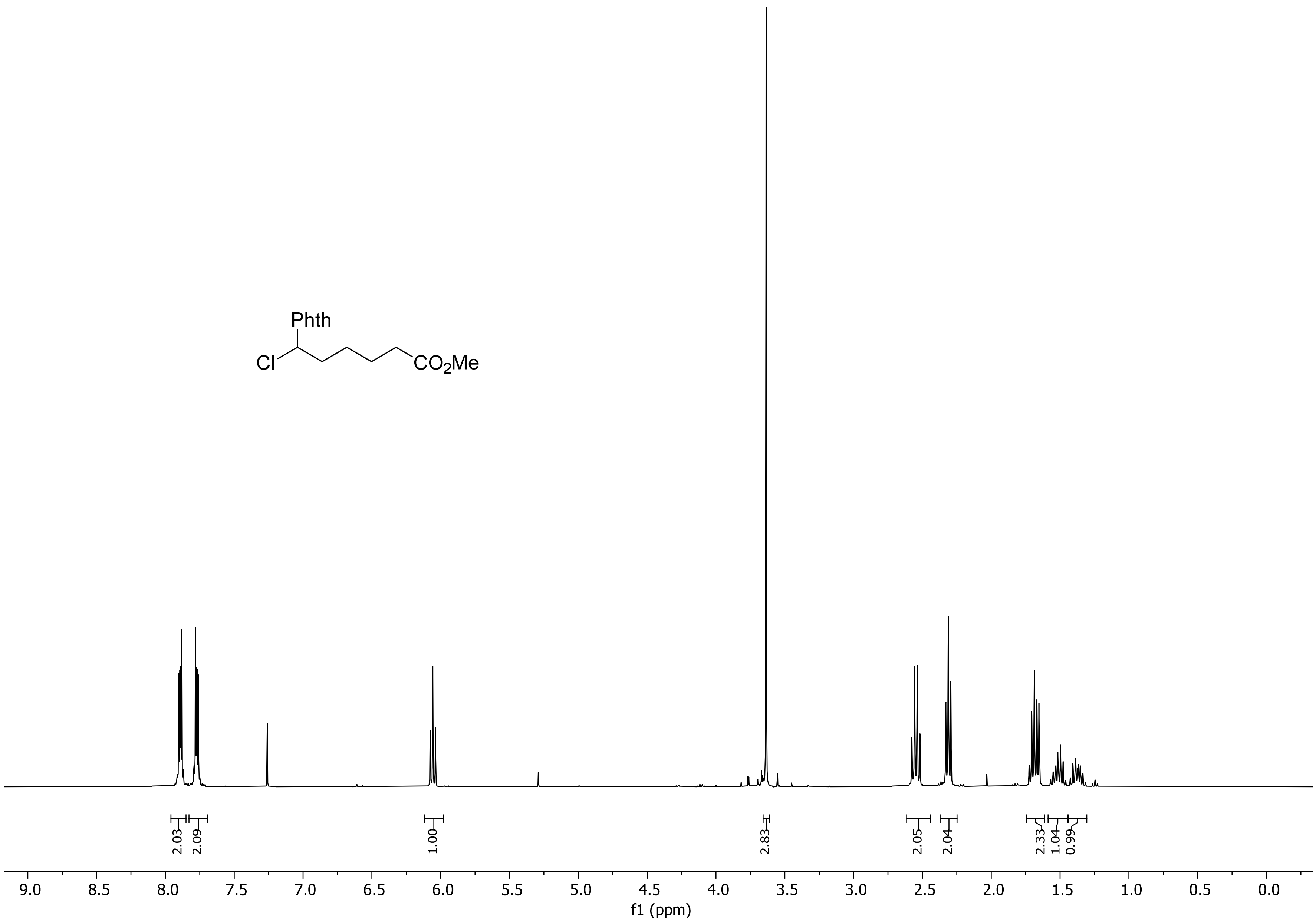
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
f1 (ppm)

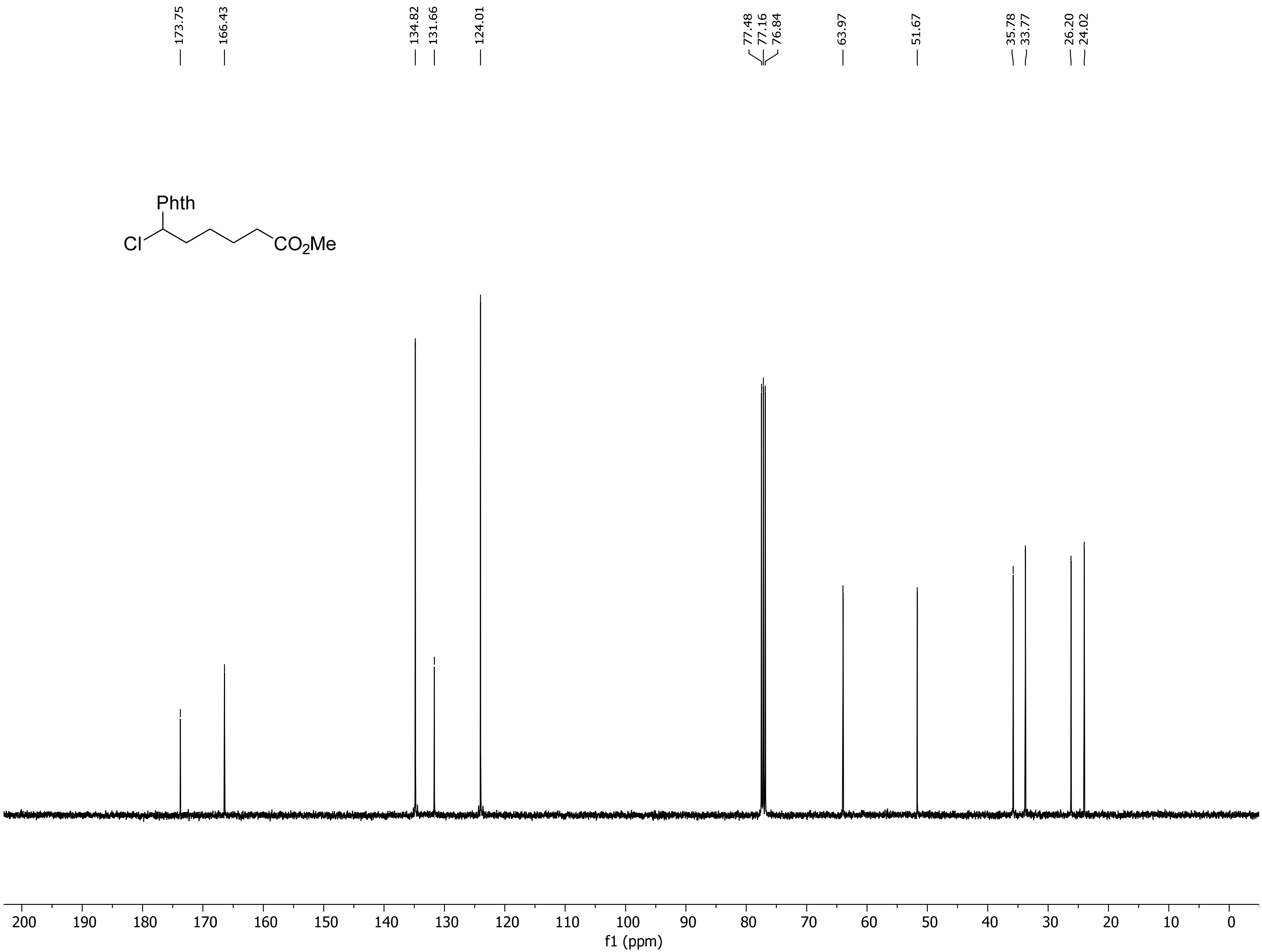

Phth
Cl
I
2.10
2.16
1.93
1.94
1.01
3.16
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.37
139.15
137.72
134.89
131.55
130.62
123.97
91.65
77.48
77.16
76.84
63.47
36.99
32.59
Phth
Cl
I
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

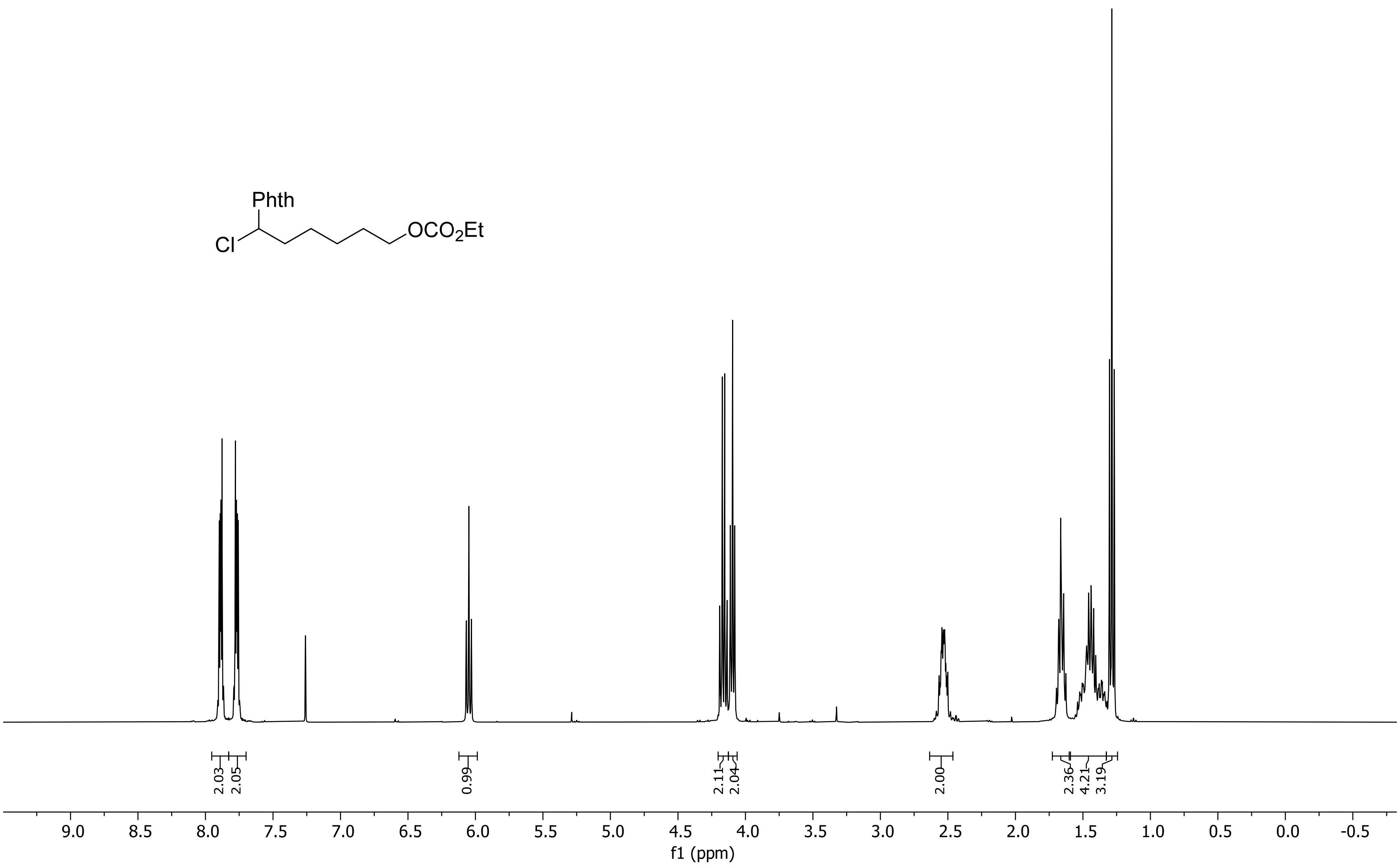

Phth
Cl
OPiv
1.95
1.97
1.00
2.18
2.00
2.18
4.32
9.40
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

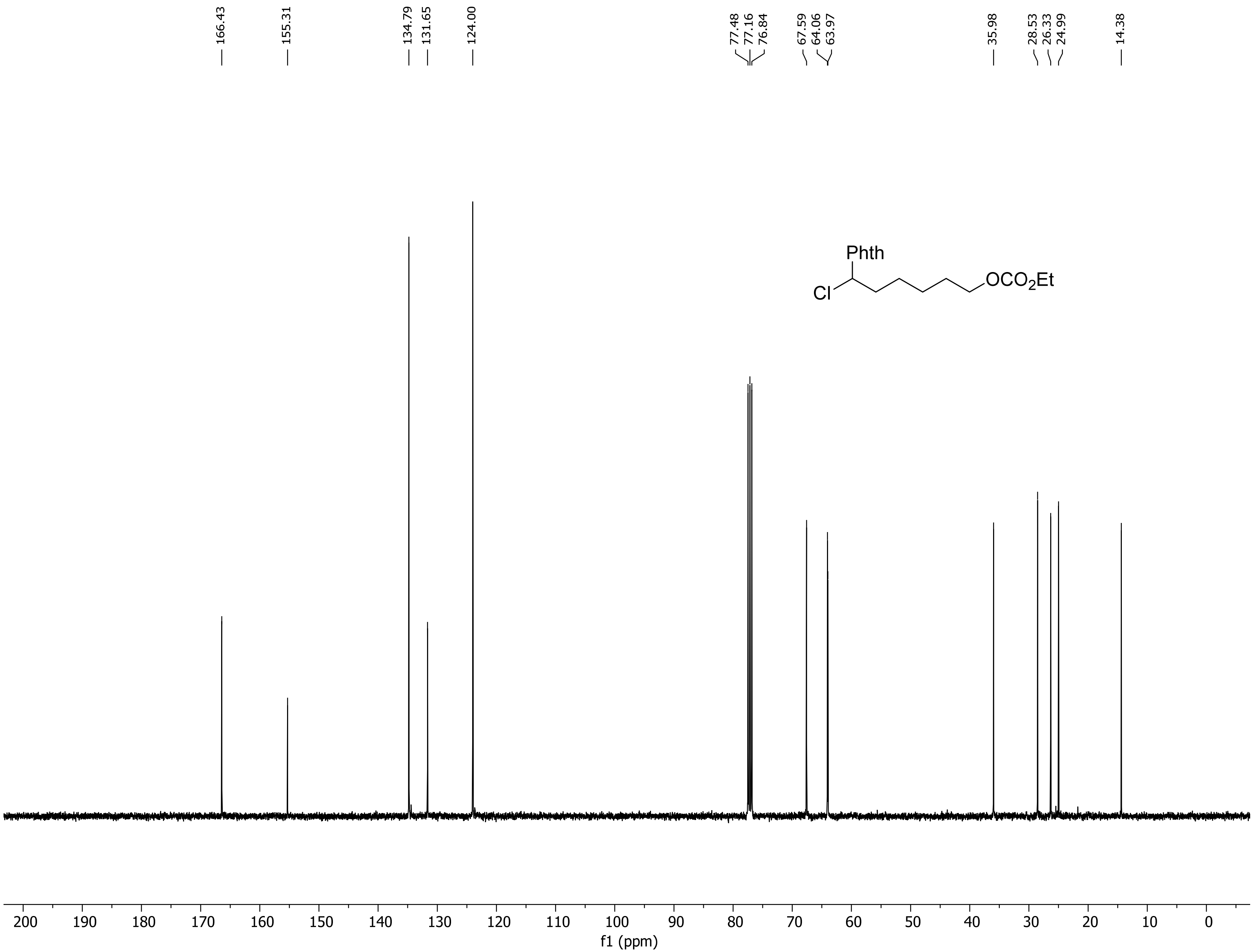

178.69
166.45
134.81
131.66
124.01
77.48
77.16
76.84
64.15
64.08
38.83
36.05
28.51
27.30
26.40
25.24
Phth
Cl
OPiv
0.16
0.34
1.22
0.39
1.11
0.61
0.59
0.18
0.62
0.64
1.99
0.58
0.59
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

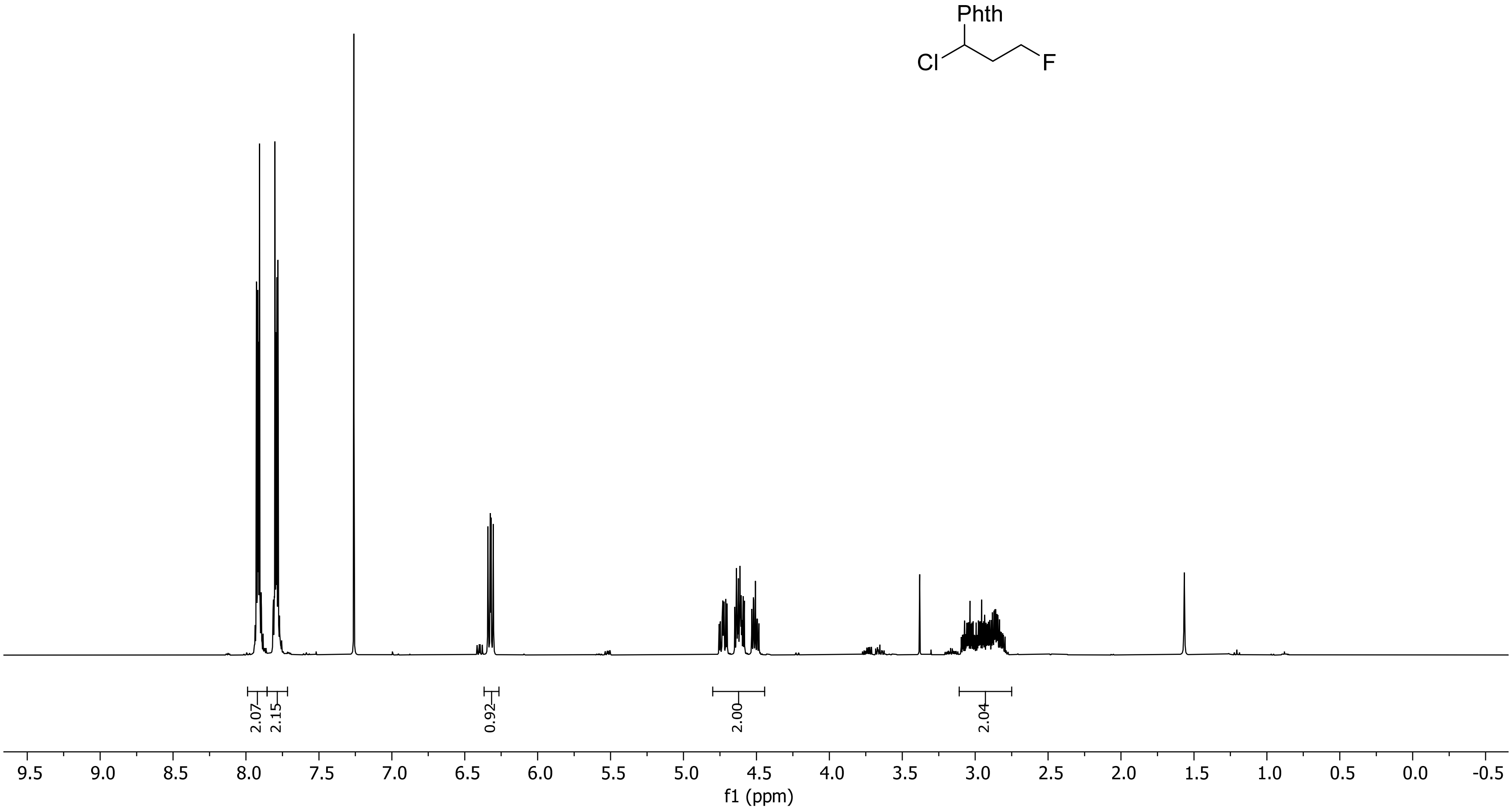

Phth
Cl
CO2Me
2.03
2.09
1.00
2.83
2.05
2.04
2.33
1.04
0.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

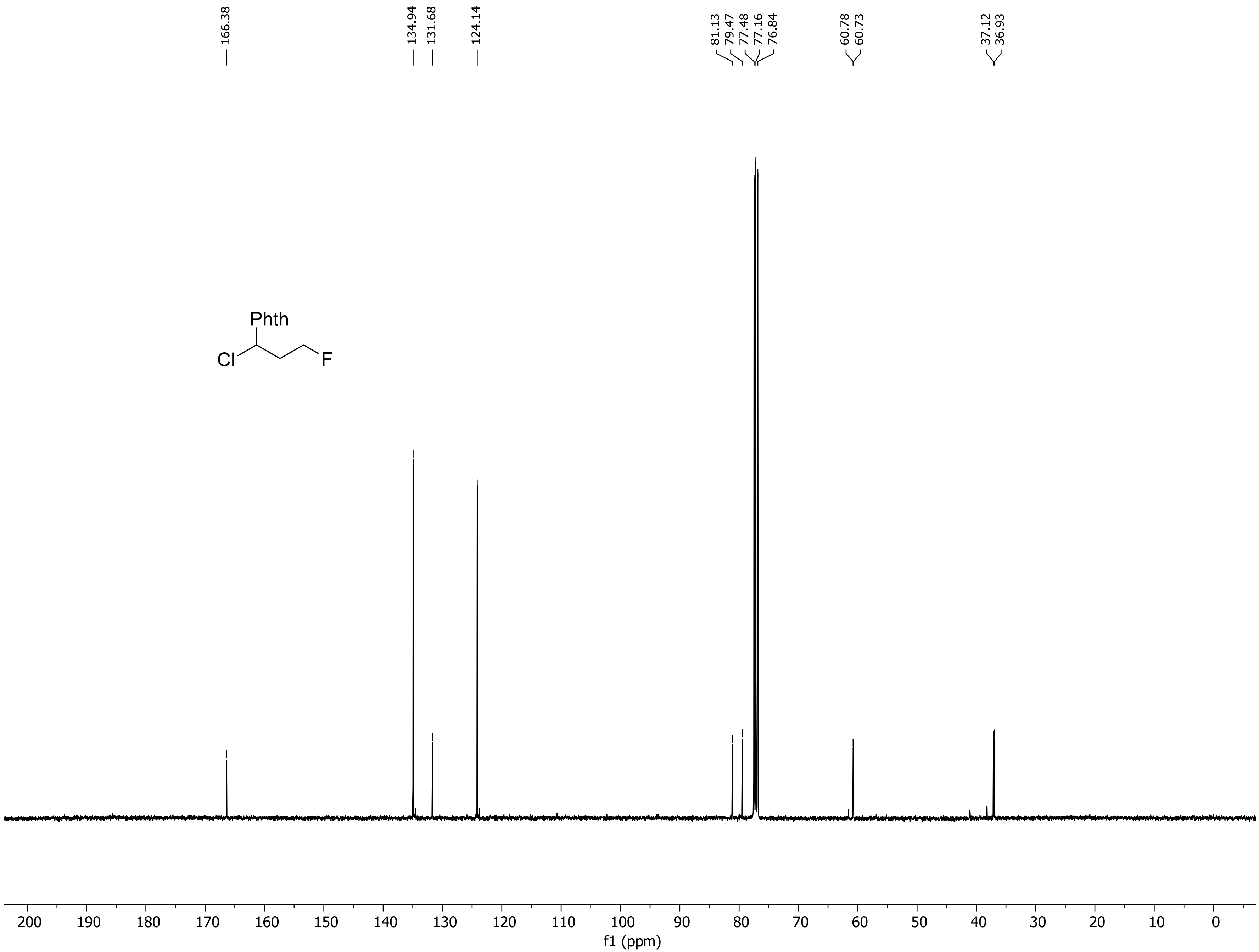


173.75
166.43
134.82
131.66
124.01
77.48
77.16
76.84
63.97
51.67
35.78
33.77
26.20
24.02
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

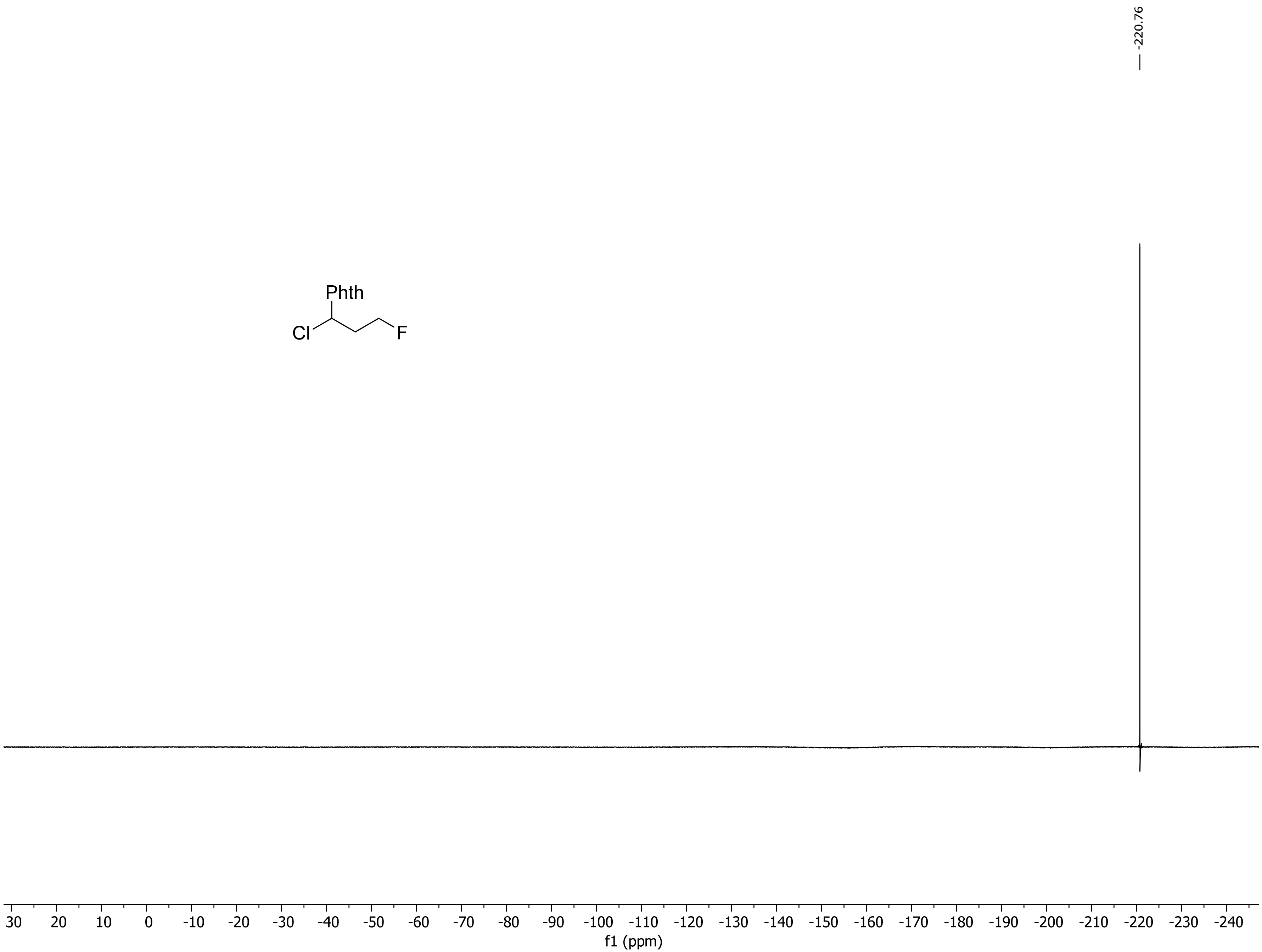

Phth
Cl
OCO2Et
2.03
2.05
0.99
2.11
2.04
2.00
2.36
4.21
3.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

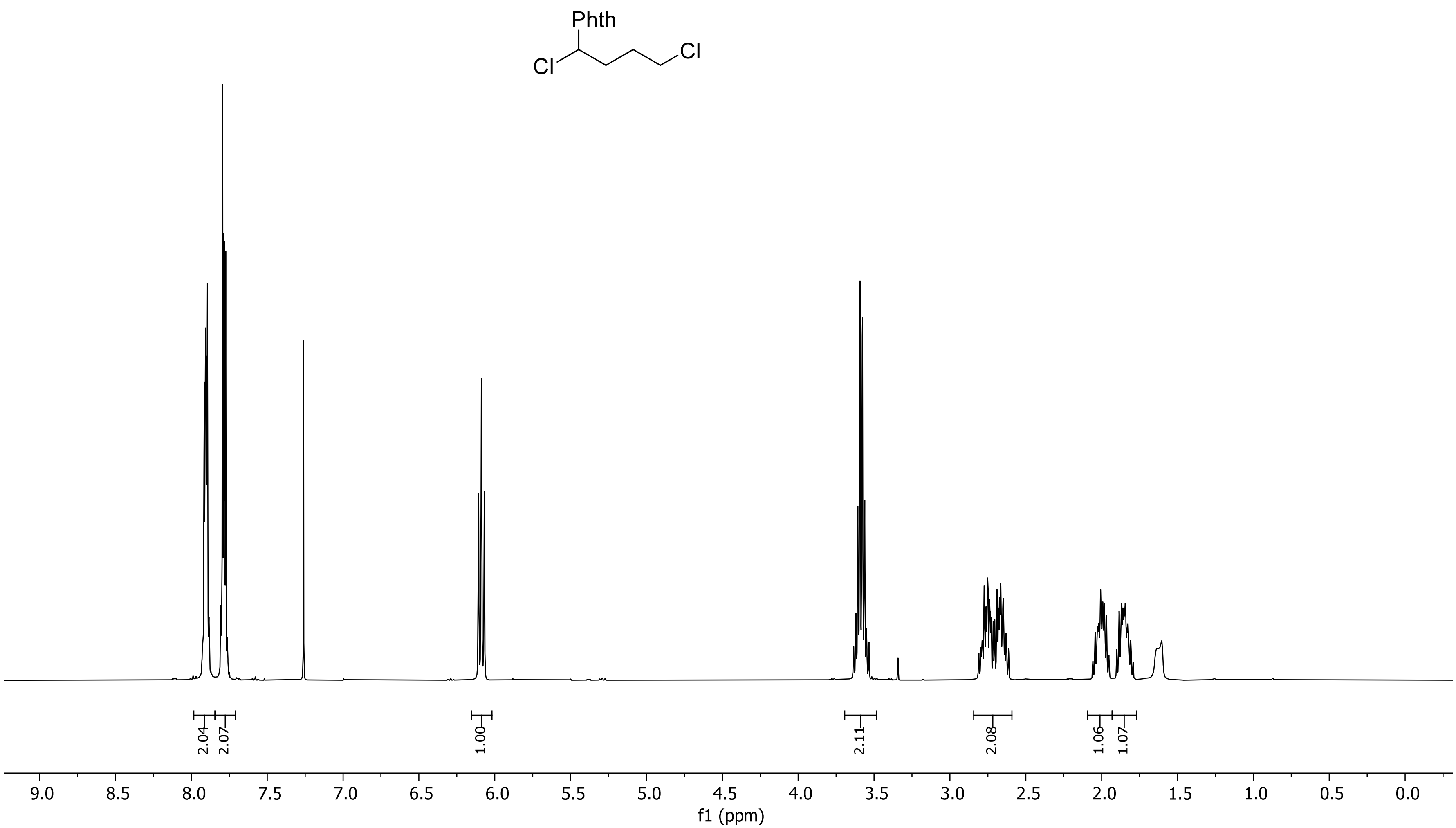

166.43
155.31
134.79
131.65
124.00
77.48
77.16
76.84
67.59
64.06
63.97
35.98
28.53
26.33
24.99
14.38
Phth
Cl
OCO2Et
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

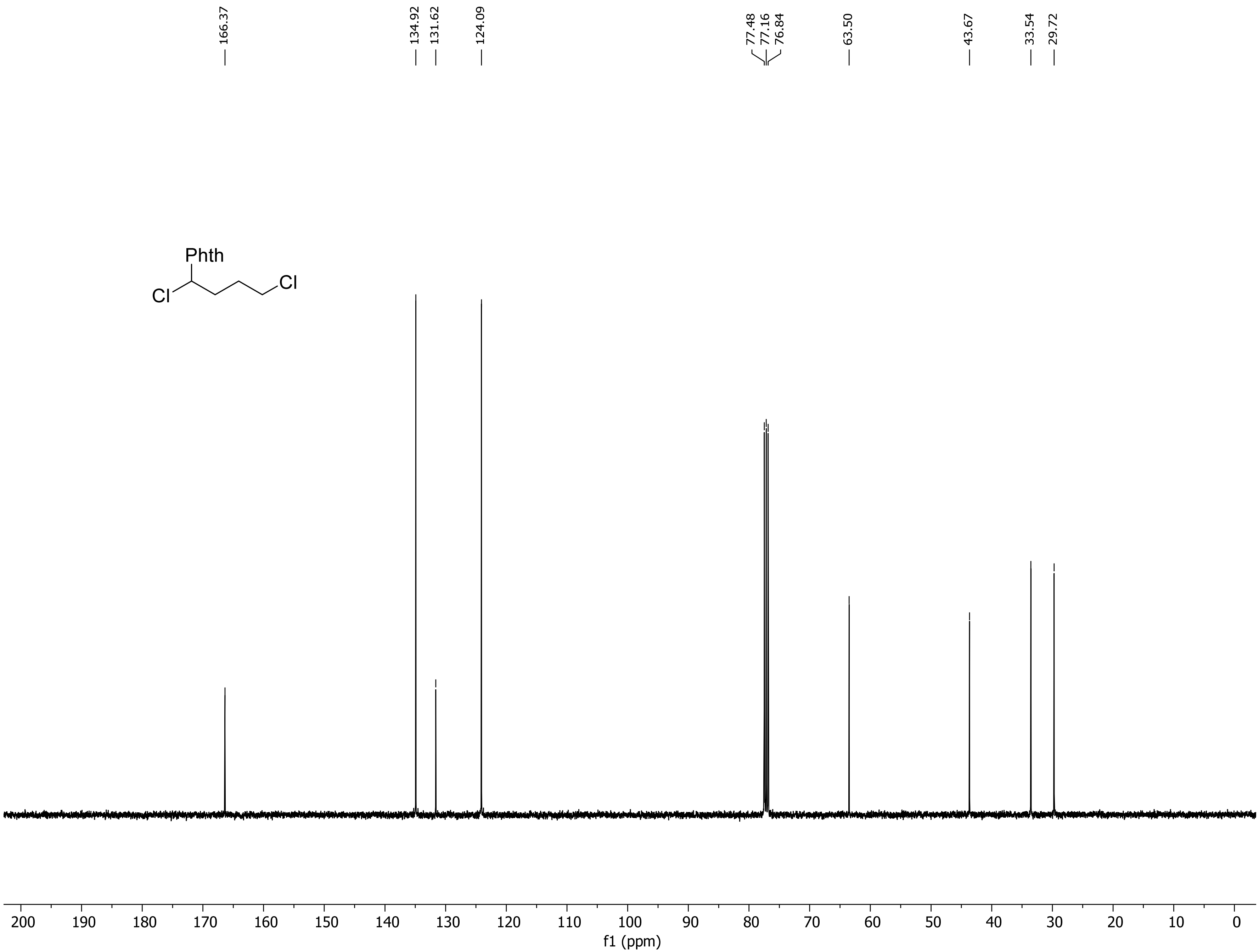

Phth
Cl
F
2.07
2.15
0.92
2.00
2.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

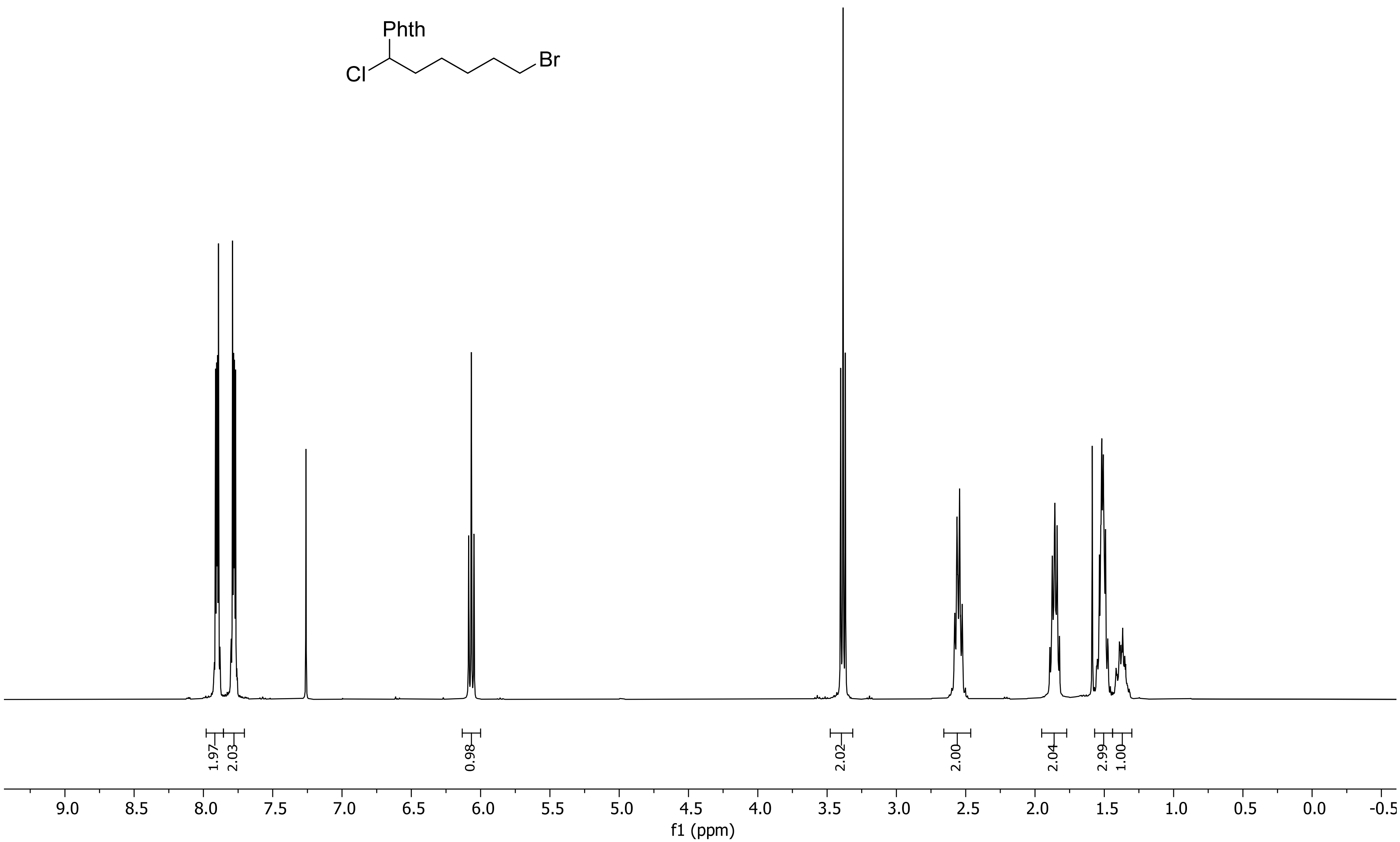


166.38
134.94
131.68
124.14
81.13
79.47
77.48
77.16
76.84
60.78
60.73
37.12
36.93
Phth
Cl
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

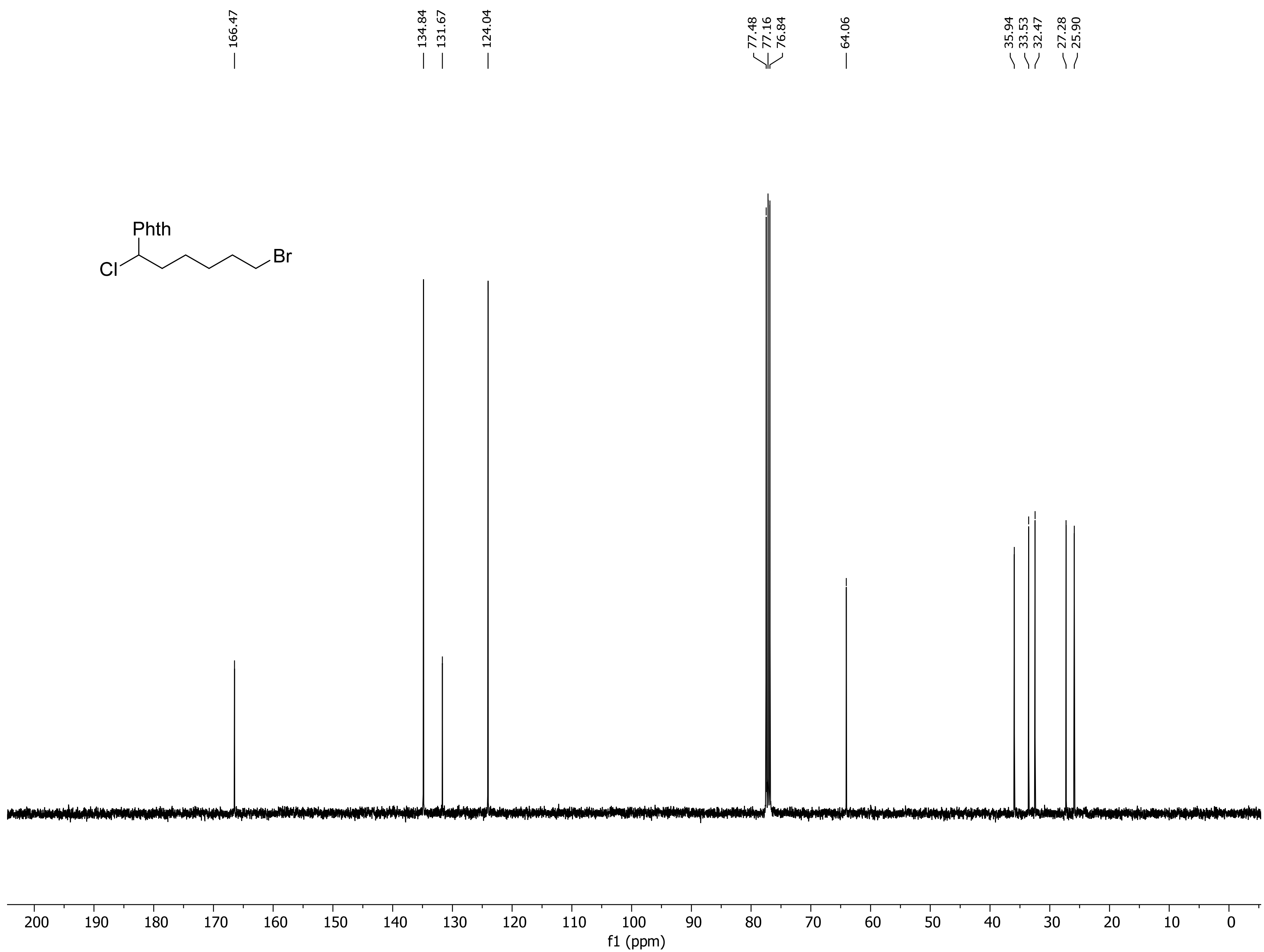

-220.76
Phth
Cl
F
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

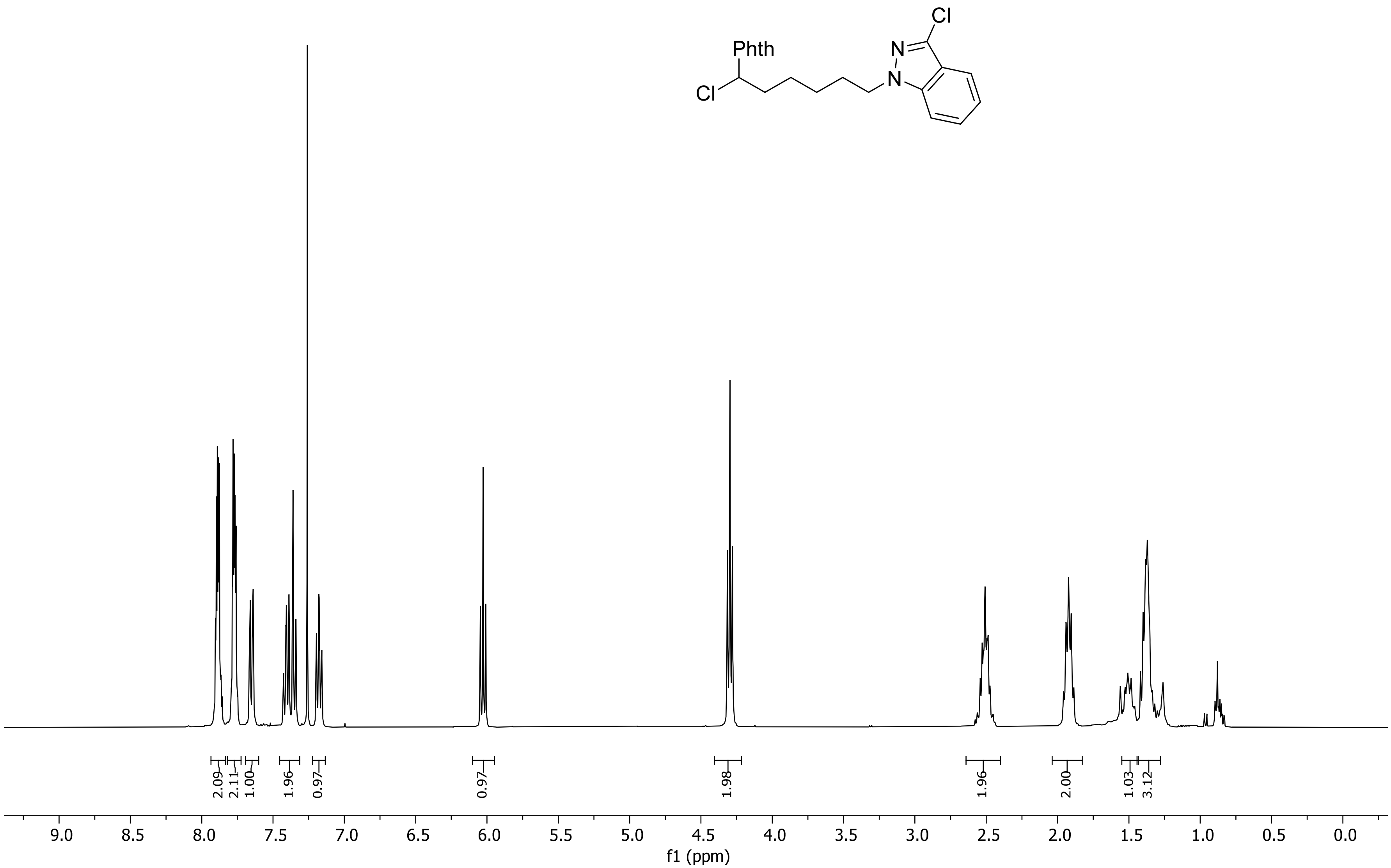

Phth
Cl
Cl
2.04
2.07
1.00
2.11
2.08
1.06
1.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

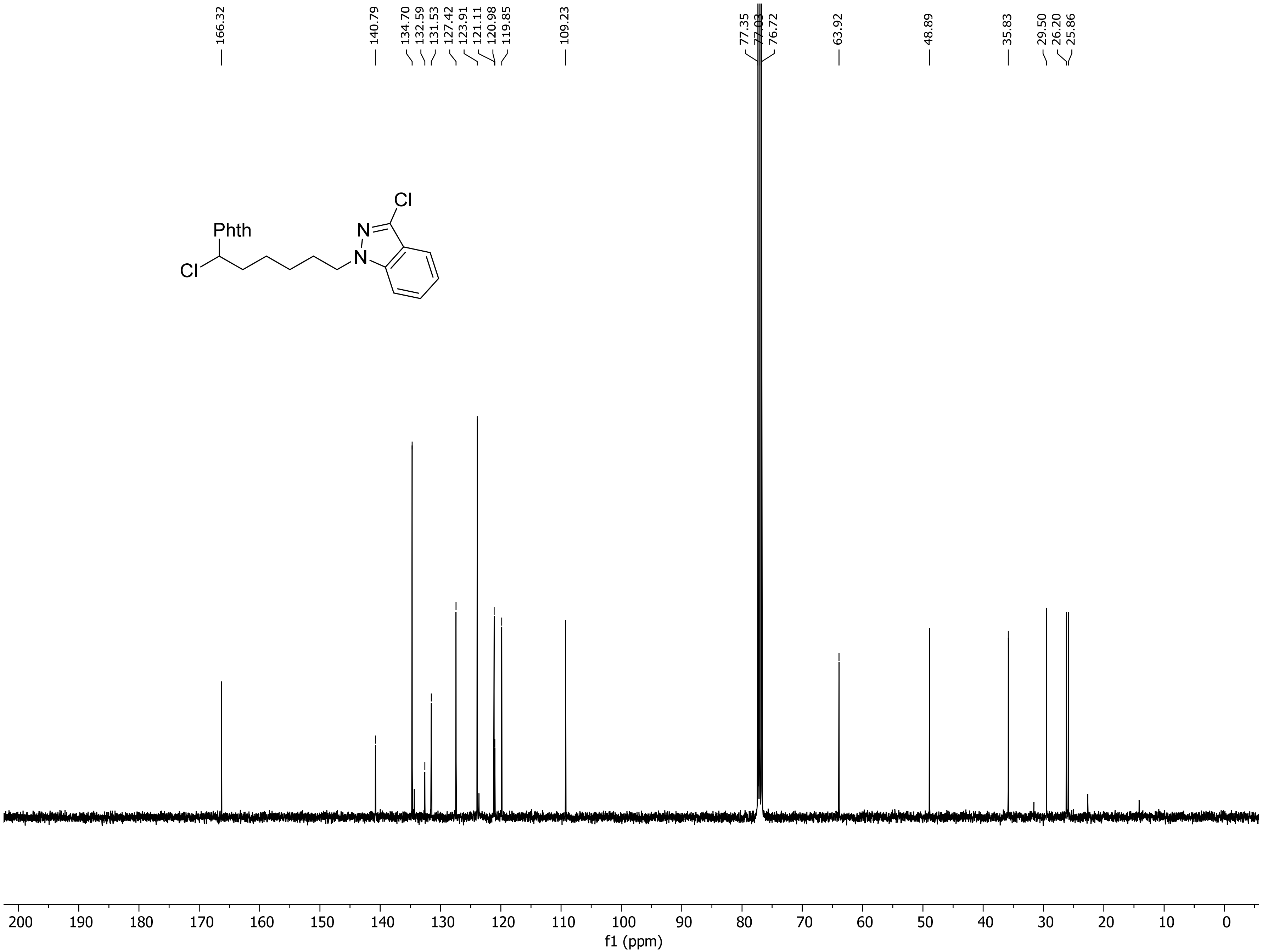

166.37
134.92
131.62
124.09
77.48
77.16
76.84
63.50
43.67
33.54
29.72
Phth
Cl
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

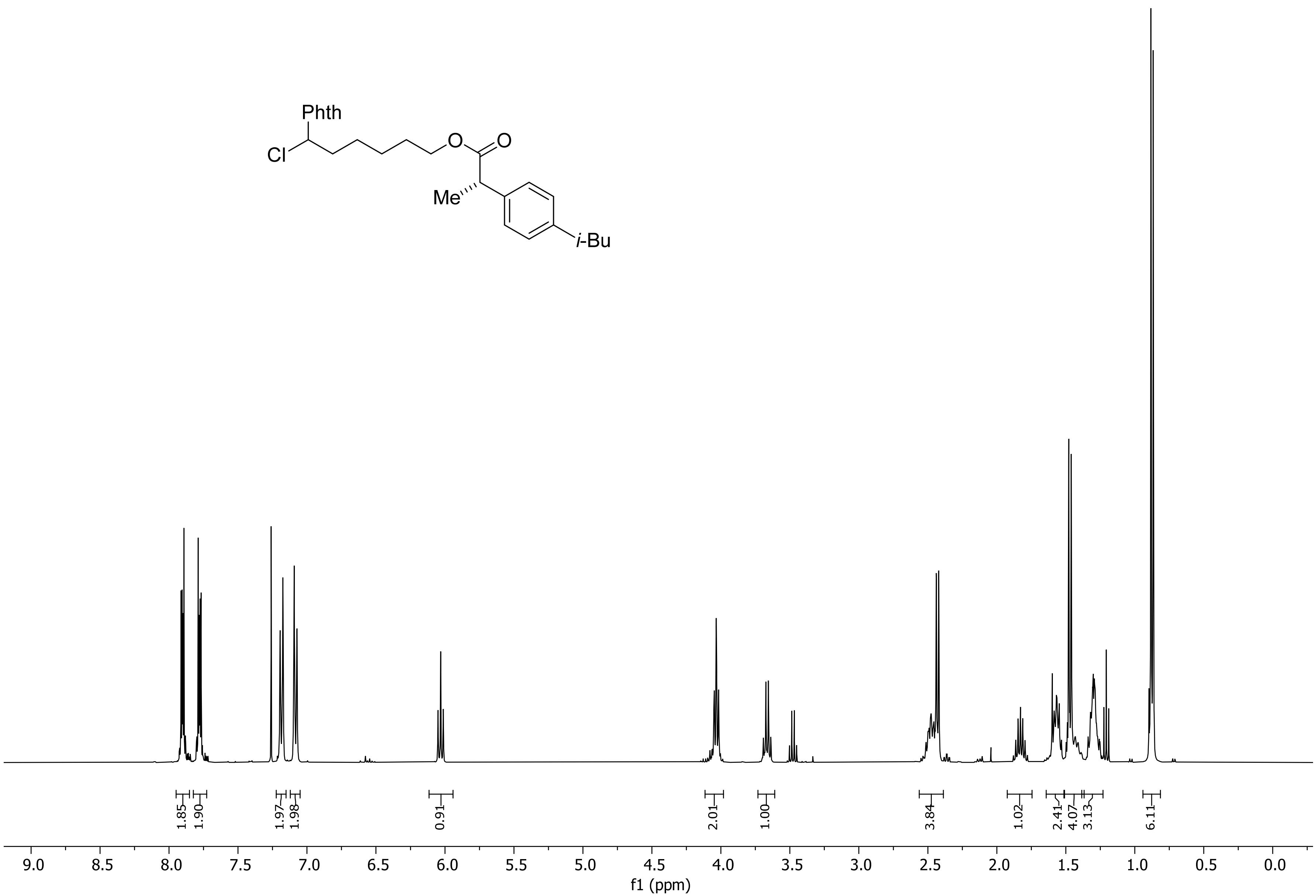


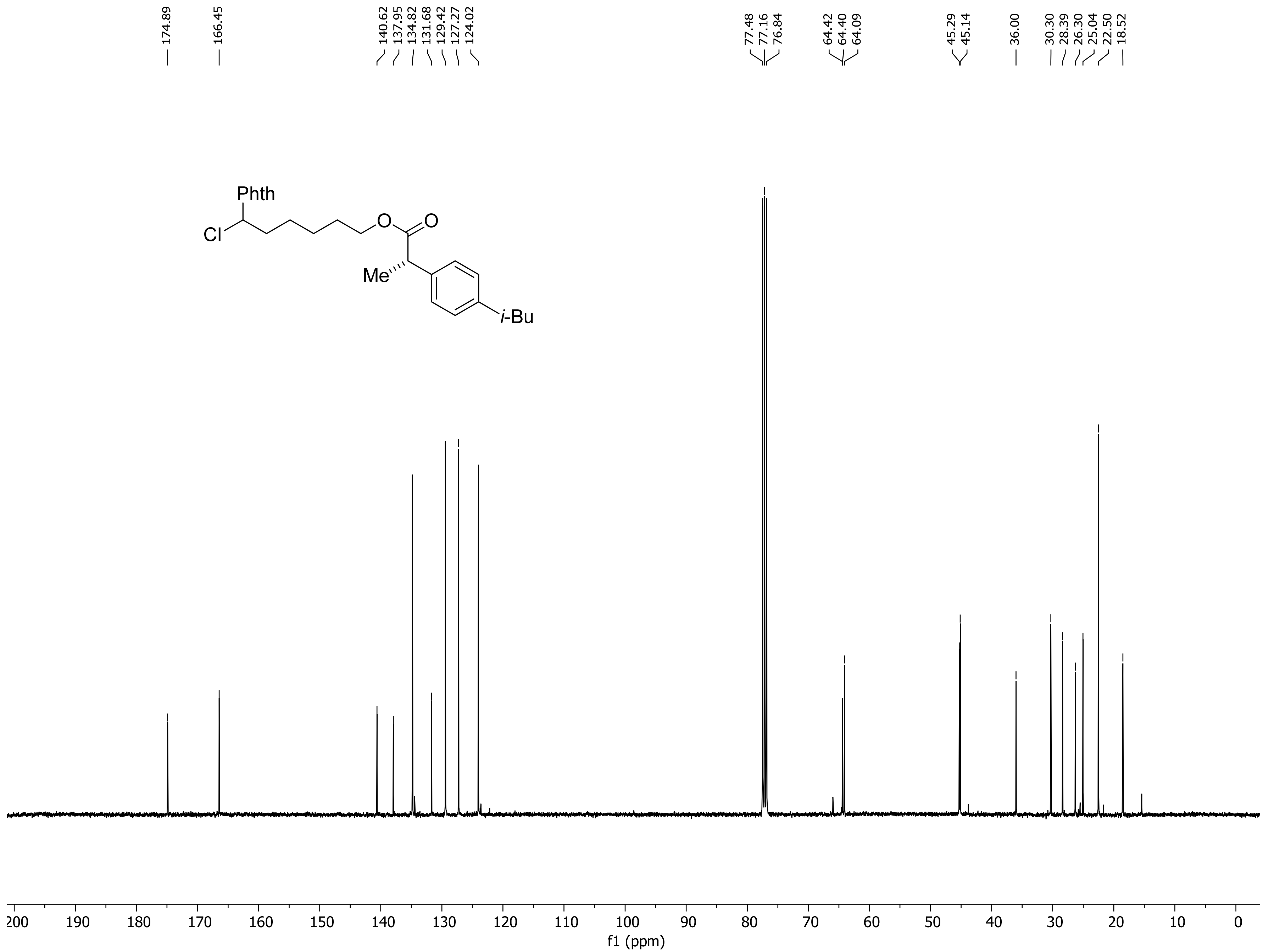
Phth
Cl
Br
1.97
2.03
0.98
2.02
2.00
2.04
2.99
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

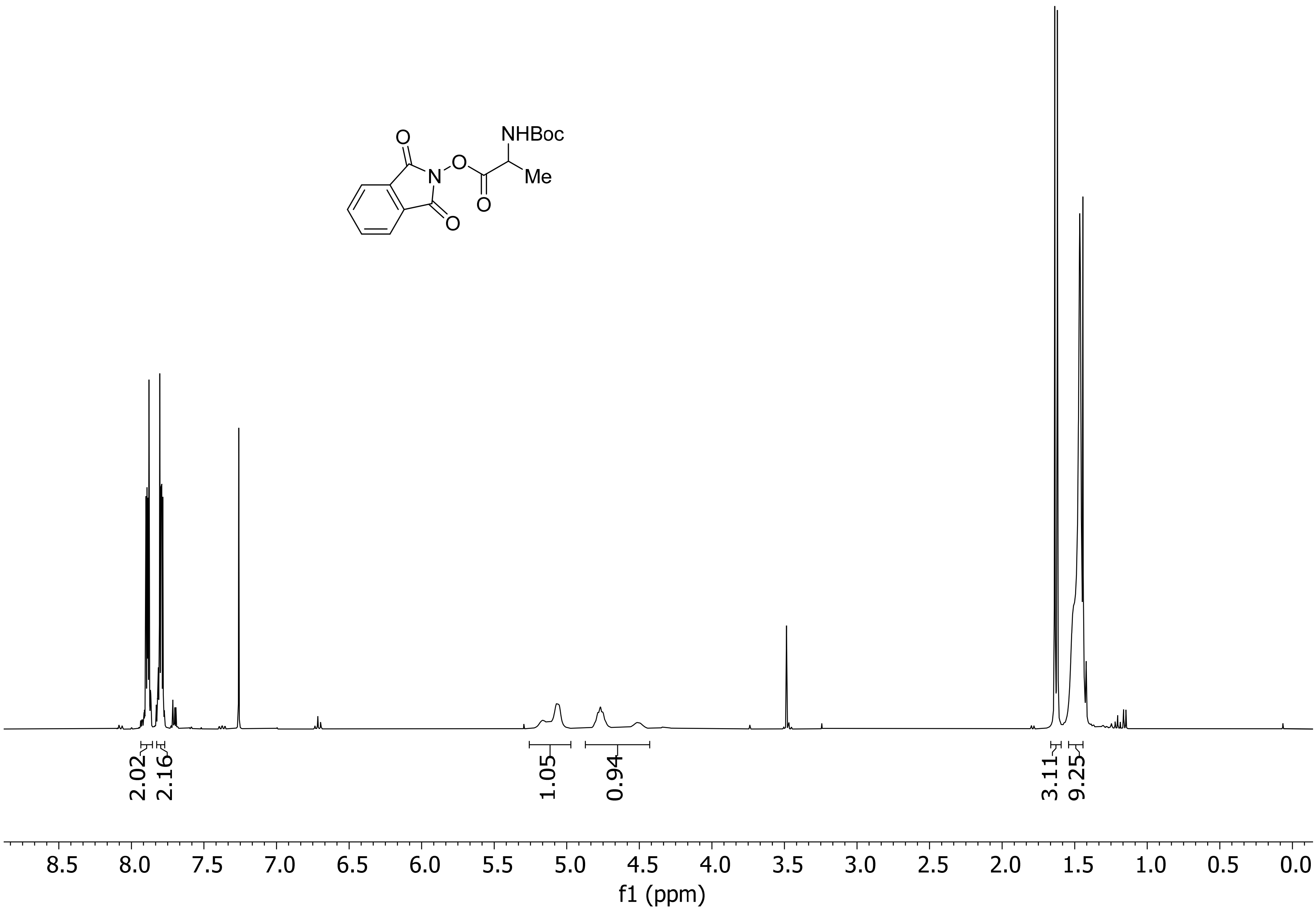

166.47
134.84
131.67
124.04
77.48
77.16
76.84
64.06
35.94
33.53
32.47
27.28
25.90
Phth
Cl
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
Phth
N
N
Cl
2.09
2.11
1.00
1.96
0.97
0.97
1.98
1.96
2.00
1.03
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

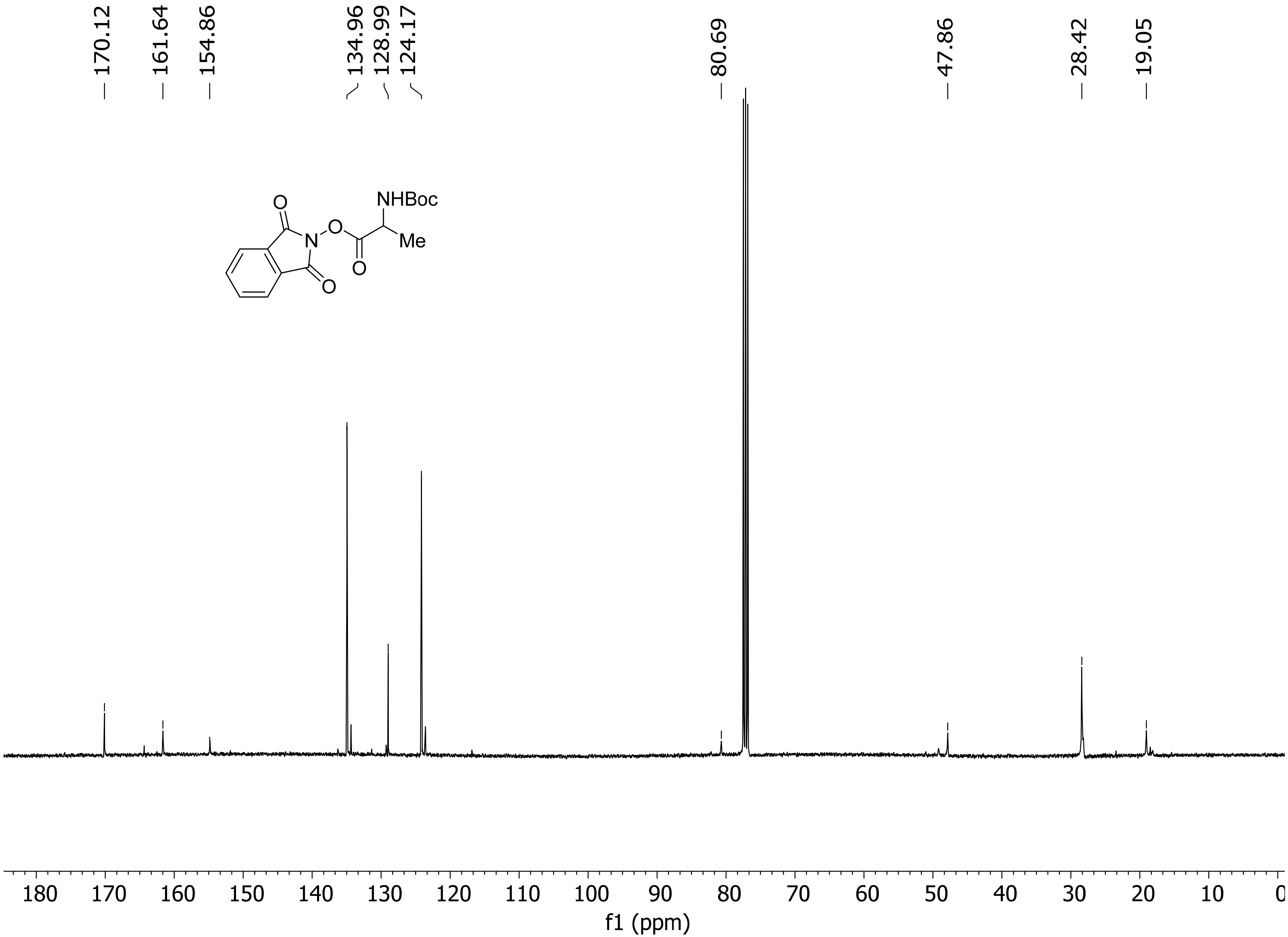

166.32
140.79
134.70
132.59
131.53
127.42
123.91
121.11
120.98
119.85
109.23
77.35
77.03
76.72
63.92
48.89
35.83
29.50
26.20
25.86
Cl
N
N
Phth
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Phth
Cl
O
O
Me
i-Bu
1.85
1.90
1.97
1.98
0.91
2.01
1.00
3.84
1.02
2.41
4.07
3.13
6.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

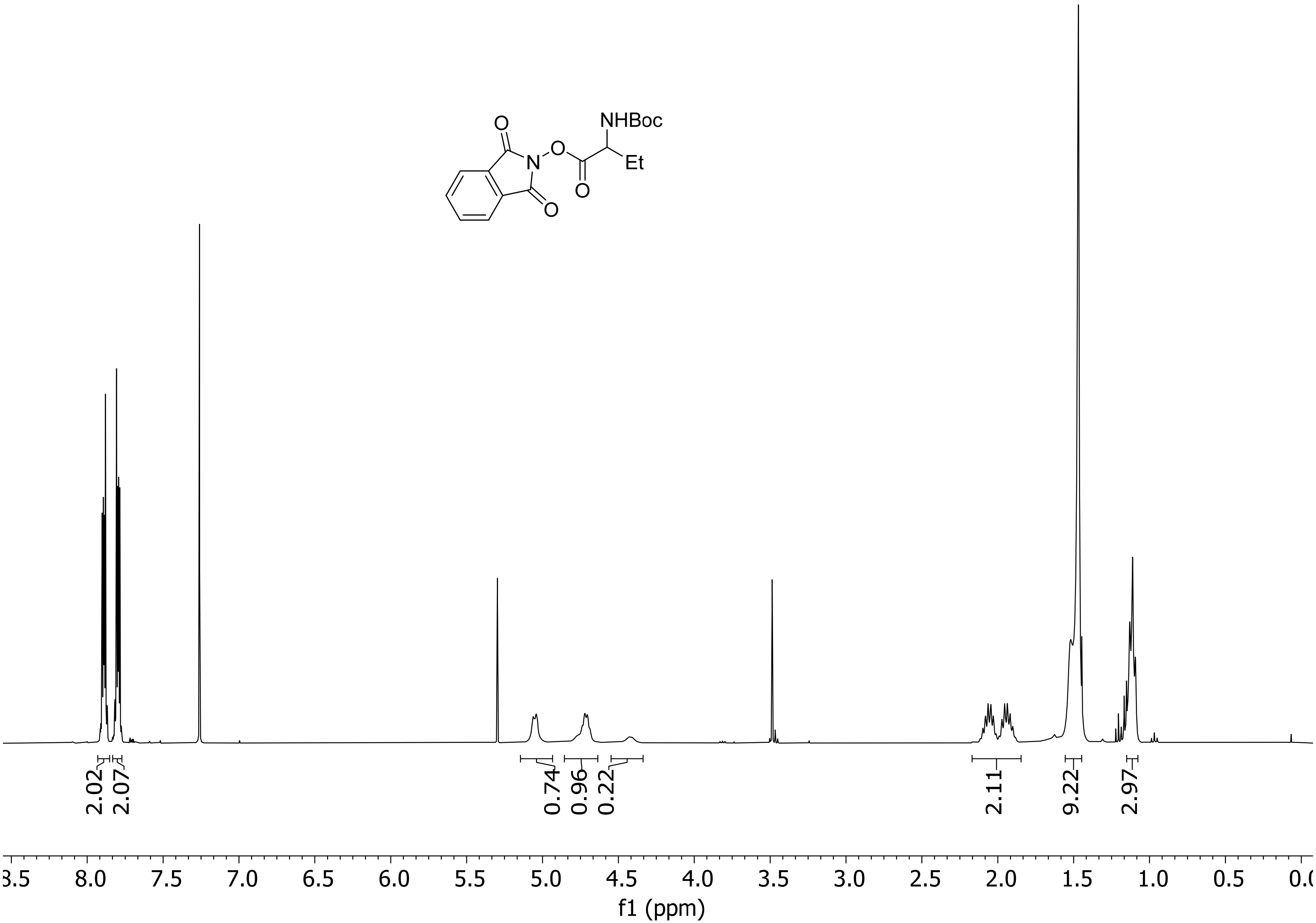

174.89
166.45
140.62
137.95
134.82
131.68
129.42
127.27
124.02
77.48
77.16
76.84
64.42
64.40
64.09
45.29
45.14
36.00
30.30
28.39
26.30
25.04
22.50
18.52
Phth
Cl
O
O
Me
i-Bu
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



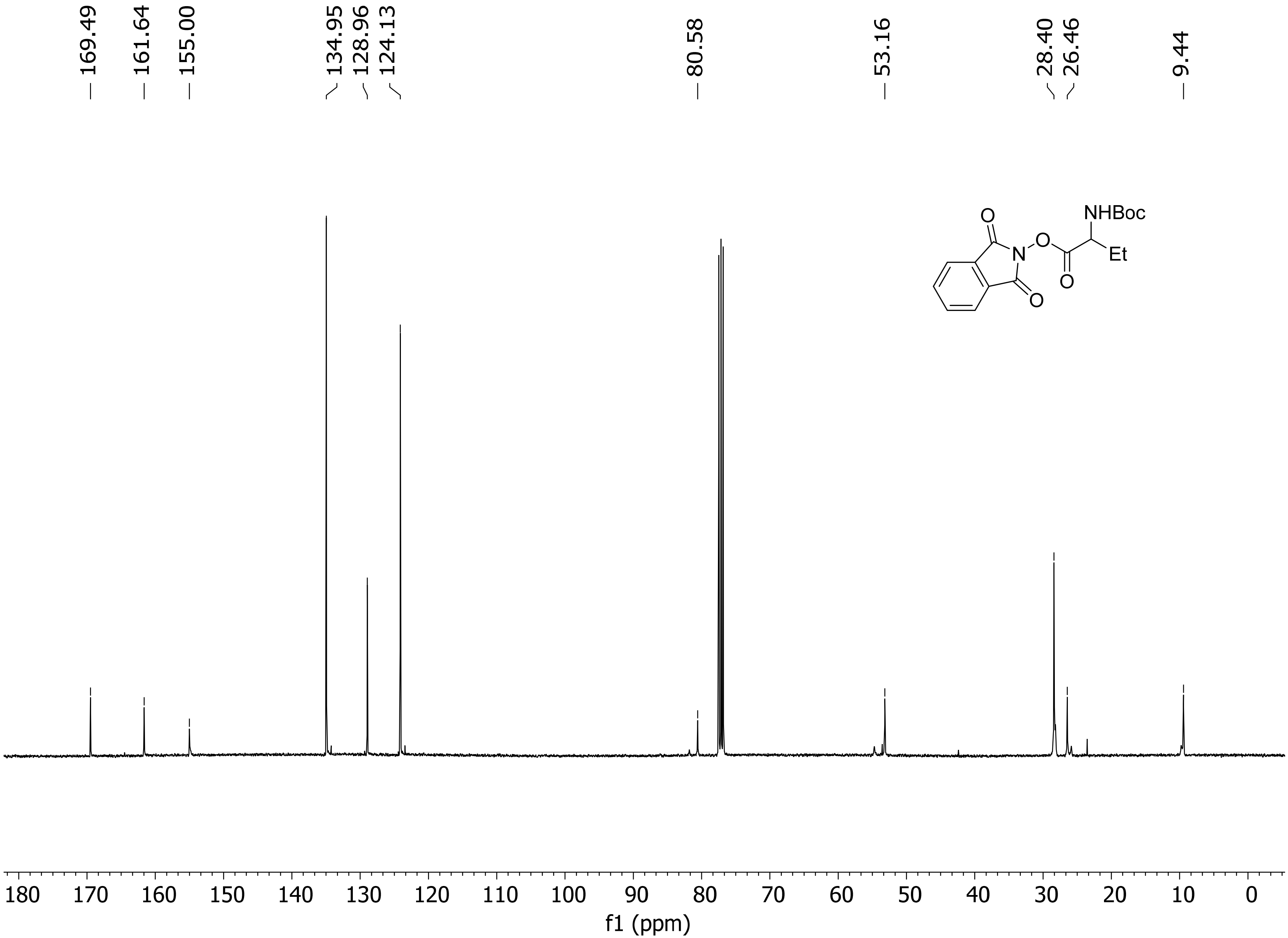
NHBoc
Me
2.02
2.16
1.05
0.94
3.11
9.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

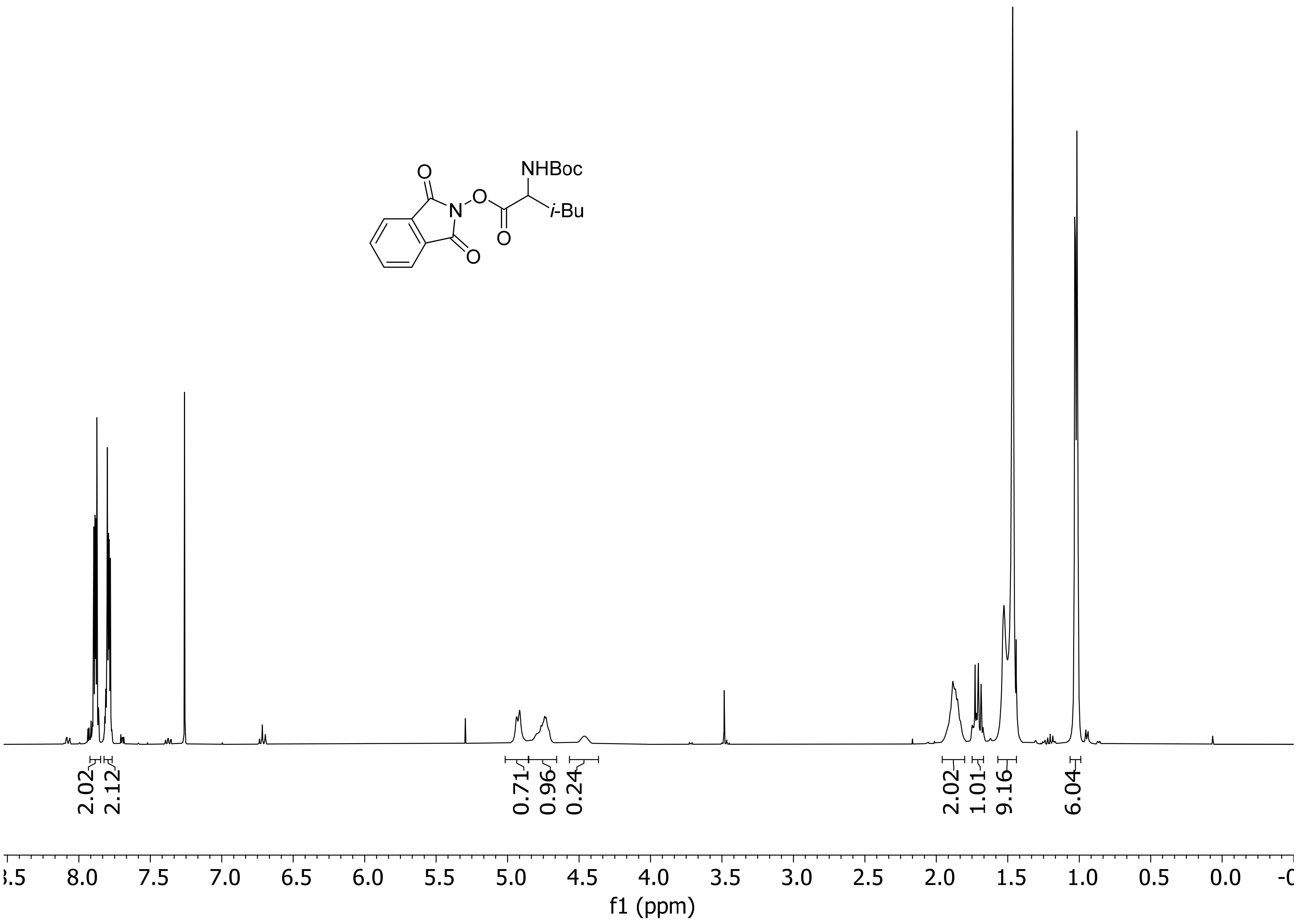


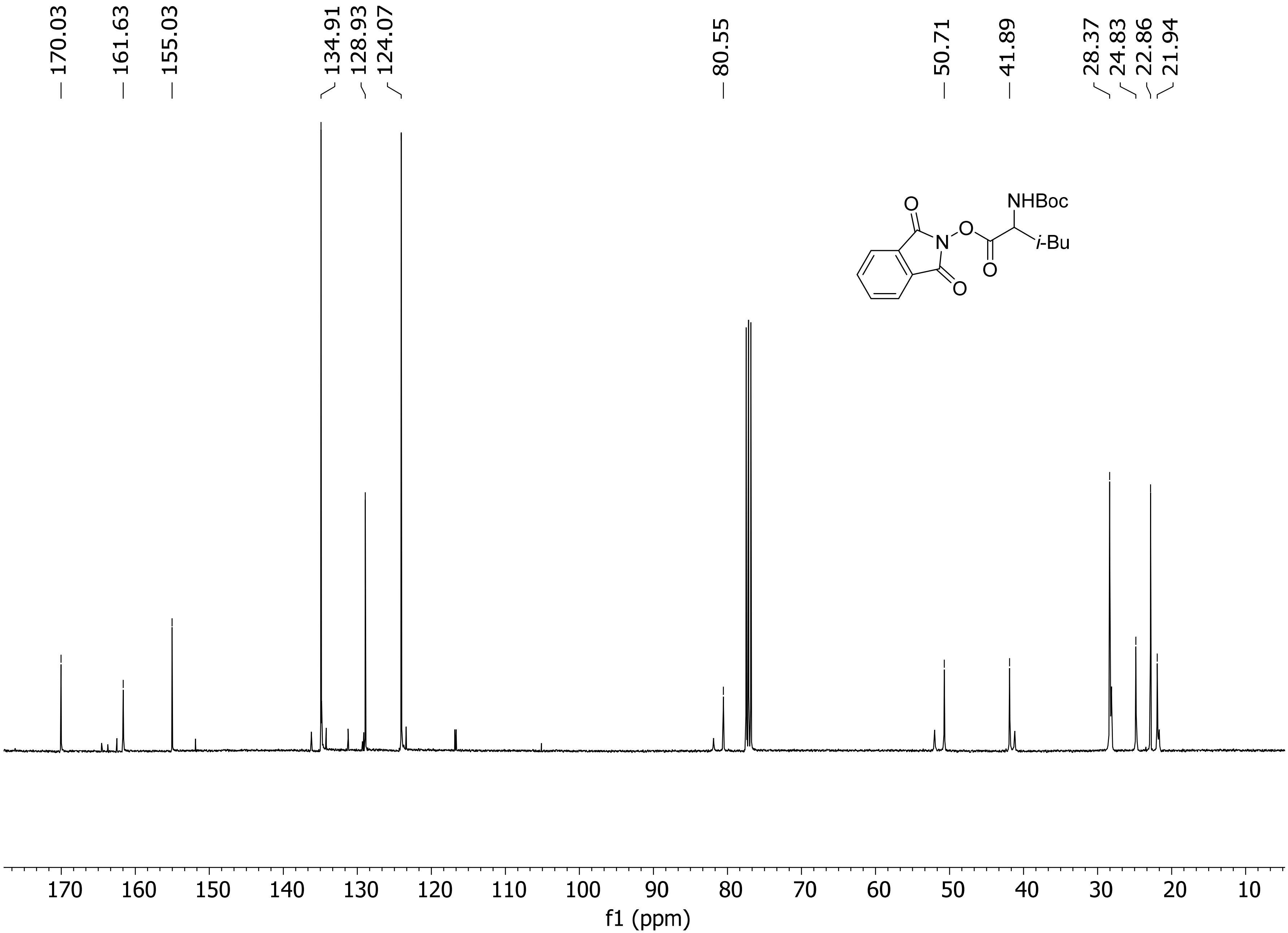
170.12
161.64
154.86
134.96
128.99
124.17
80.69
47.86
28.42
19.05
NHBoc
O
N
O
O
Me
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

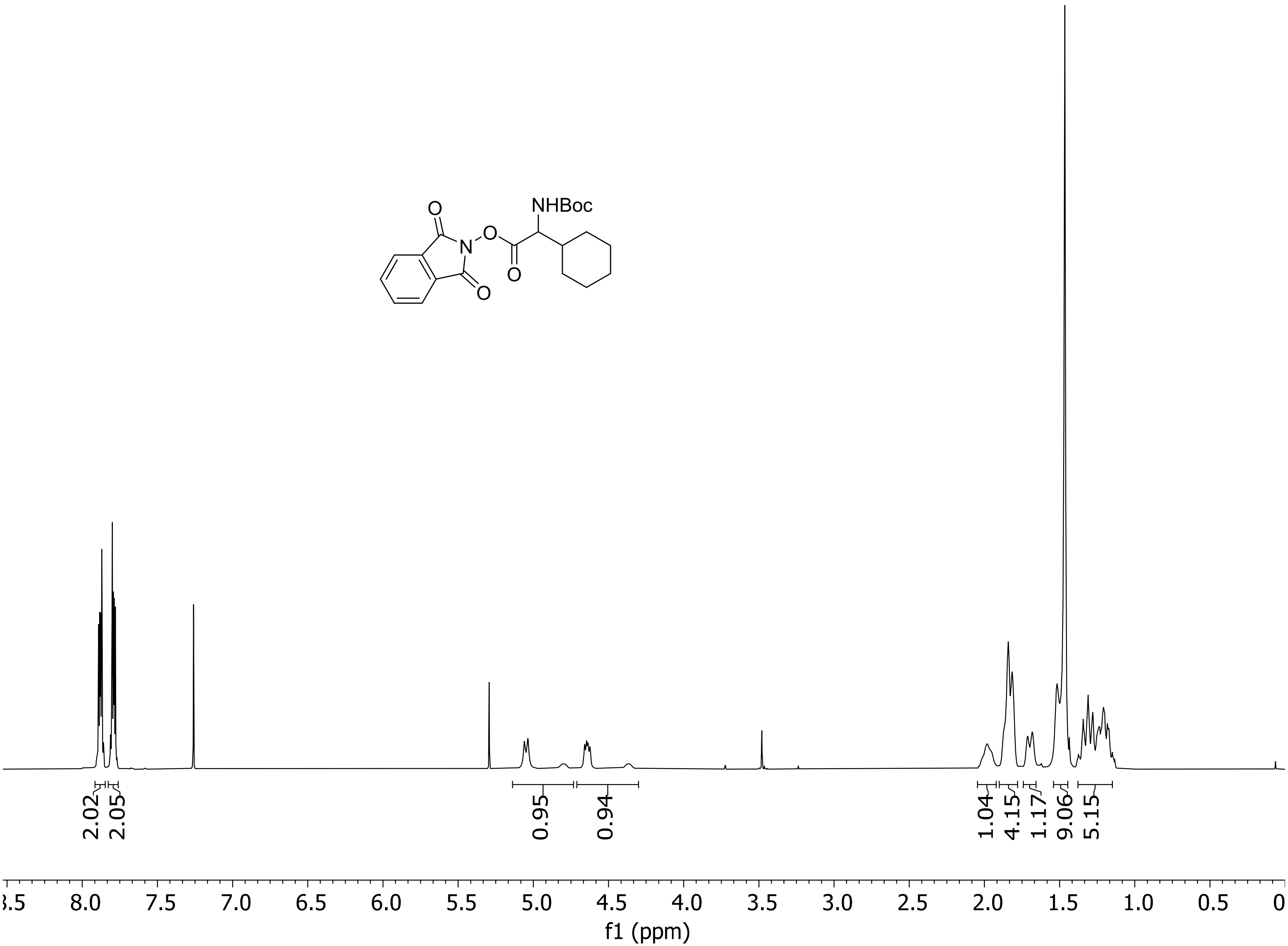


NHBoc
Et
2.02
2.07
0.74
0.96
0.22
2.11
9.22
2.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

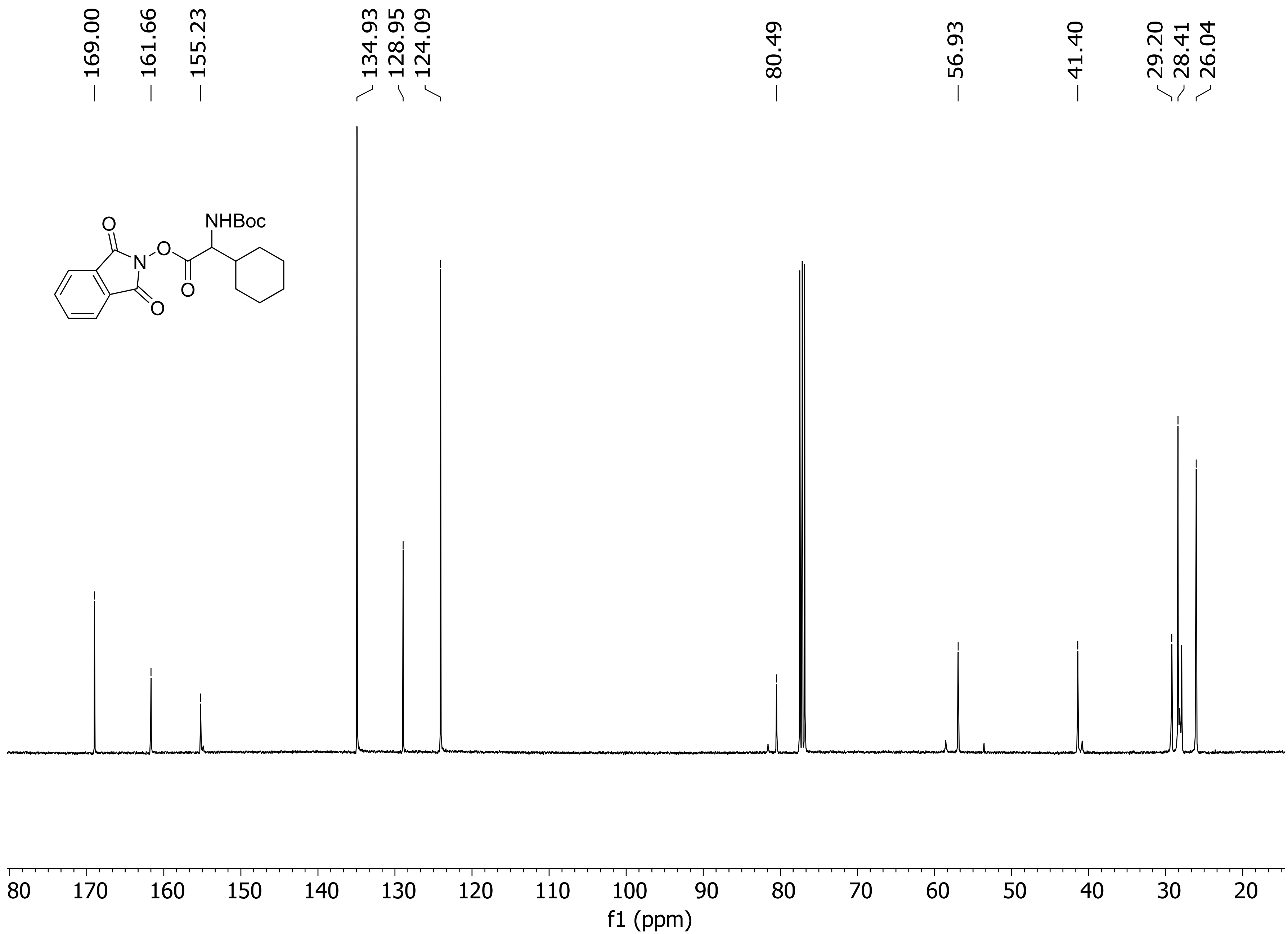

169.49
161.64
155.00
134.95
128.96
124.13
80.58
53.16
28.40
26.46
9.44
NHBoc
O
N
O
Et
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

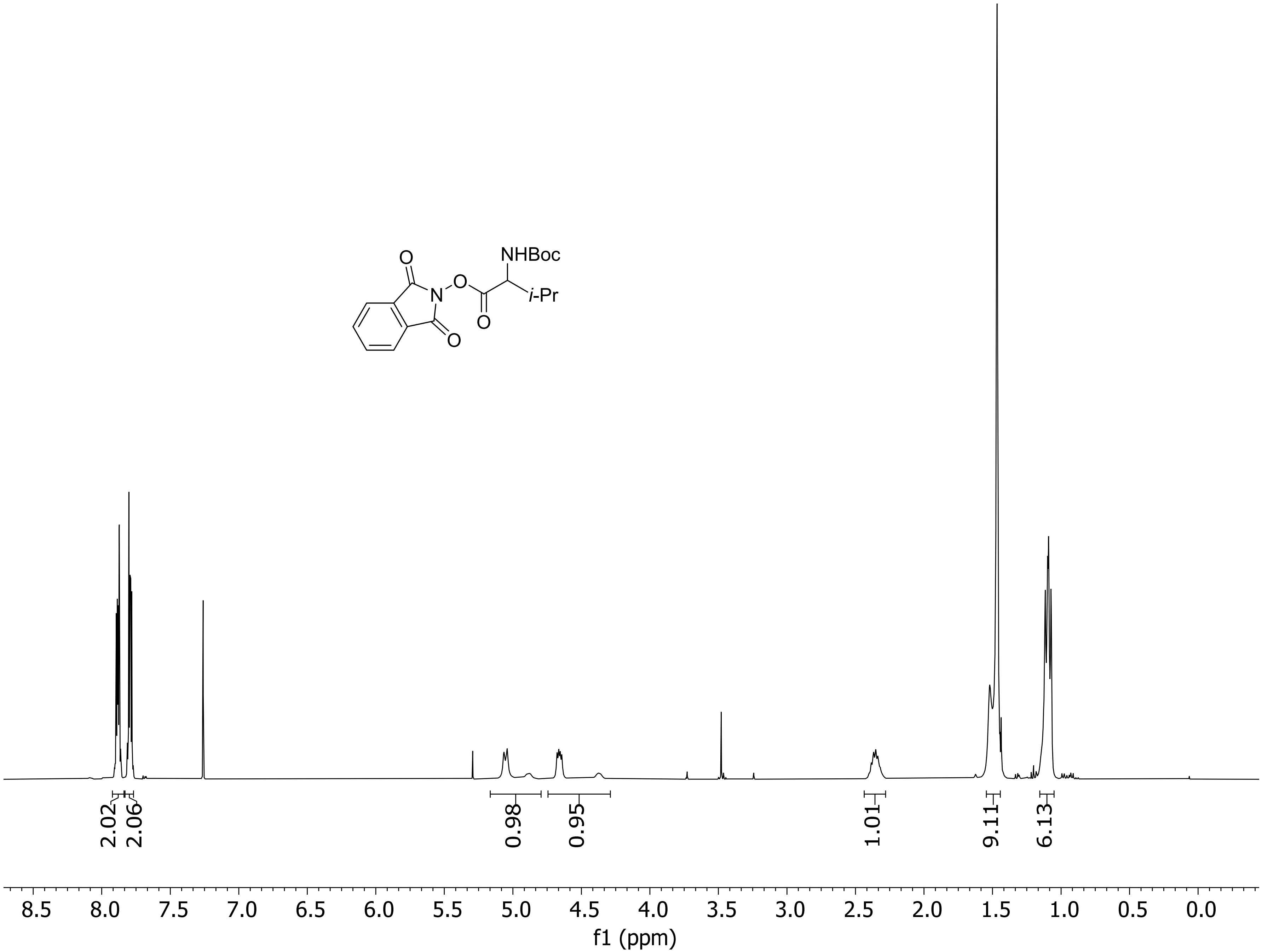

NHBoc
O
N
O
O
O
i-Bu
2.02
2.12
0.71
0.96
0.24
2.02
1.01
9.16
6.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


170.03
161.63
155.03
134.91
128.93
124.07
80.55
50.71
41.89
28.37
24.83
22.86
21.94
NHBoc
O
N
O
i-Bu
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

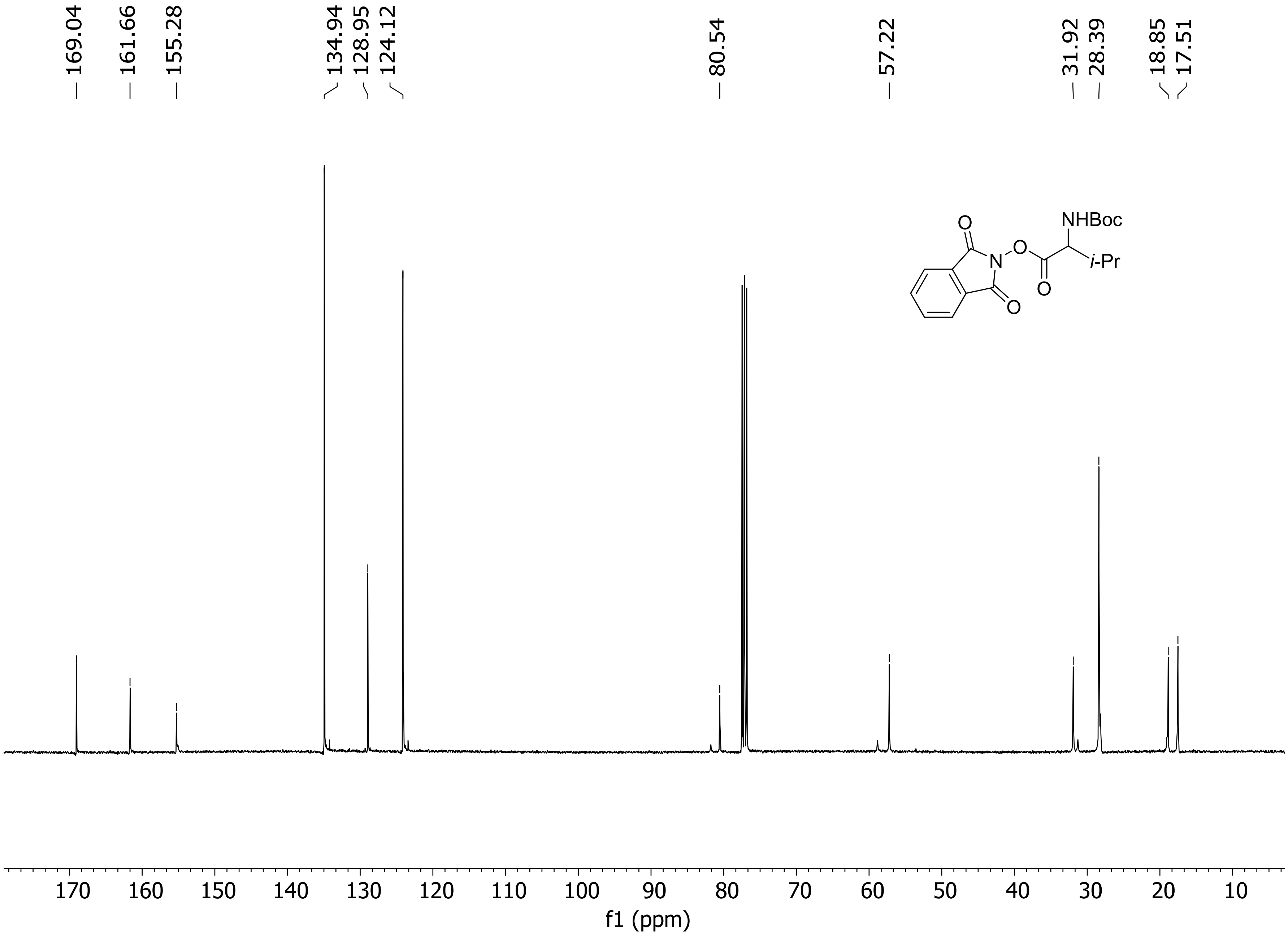


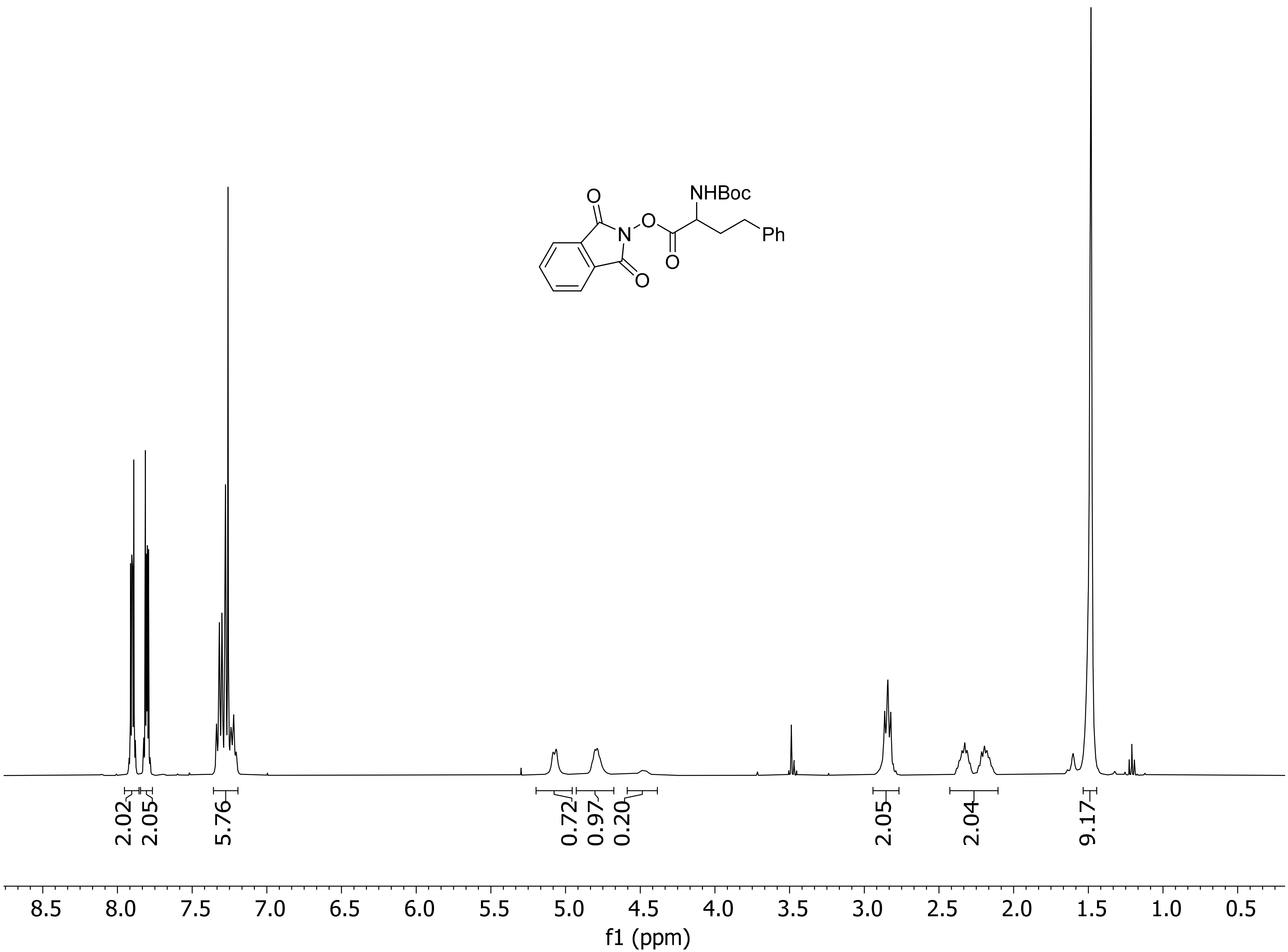
NHBoc
O
N
O
O
O
2.02
2.05
0.95
0.94
1.04
4.15
1.17
9.06
5.15
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

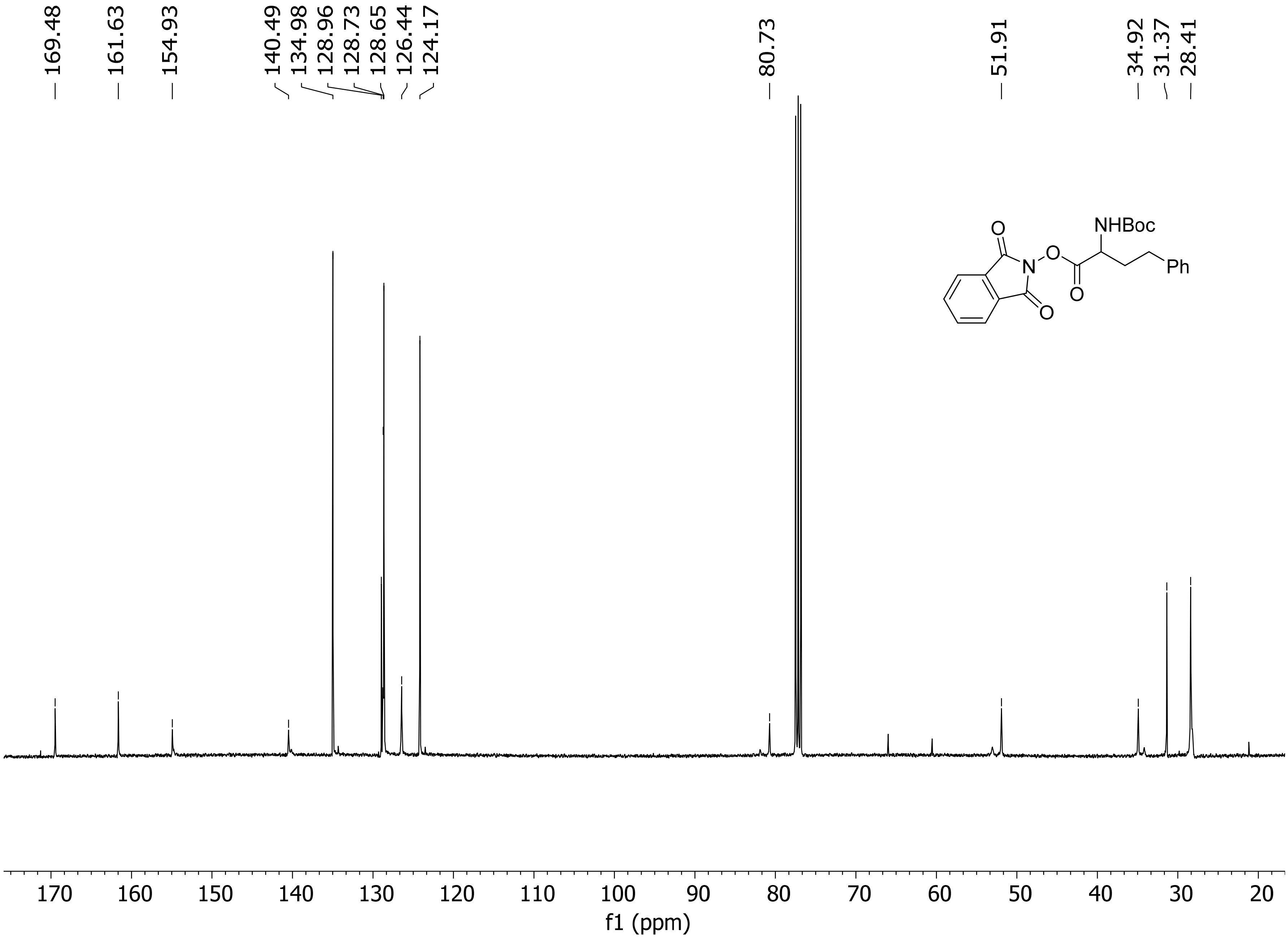

169.00
161.66
155.23
134.93
128.95
124.09
80.49
56.93
41.40
29.20
28.41
26.04
NHBoc
O
N
O
O
O
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

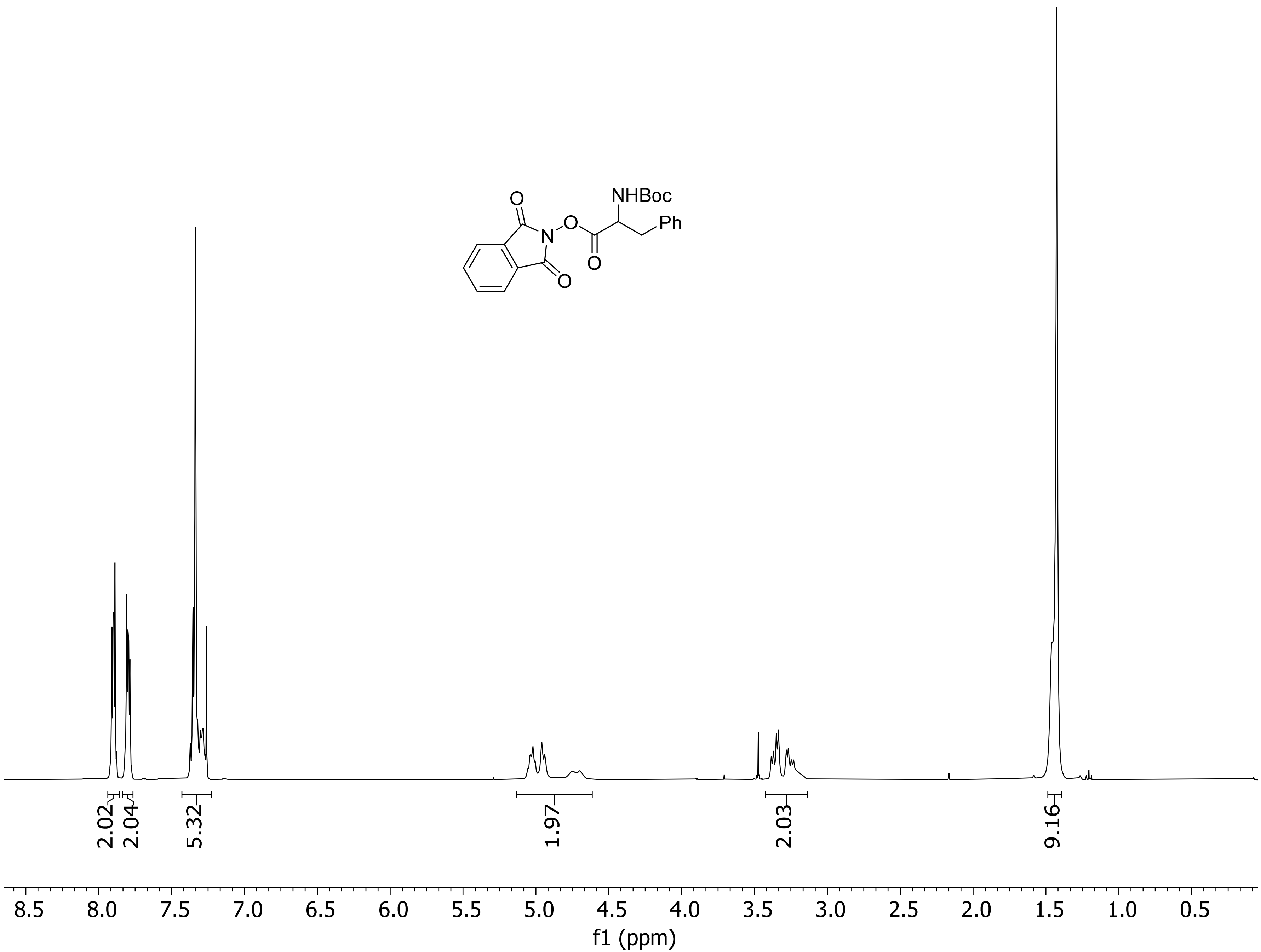


NHBoc
i-Pr
2.02
2.06
0.98
0.95
1.01
9.11
6.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

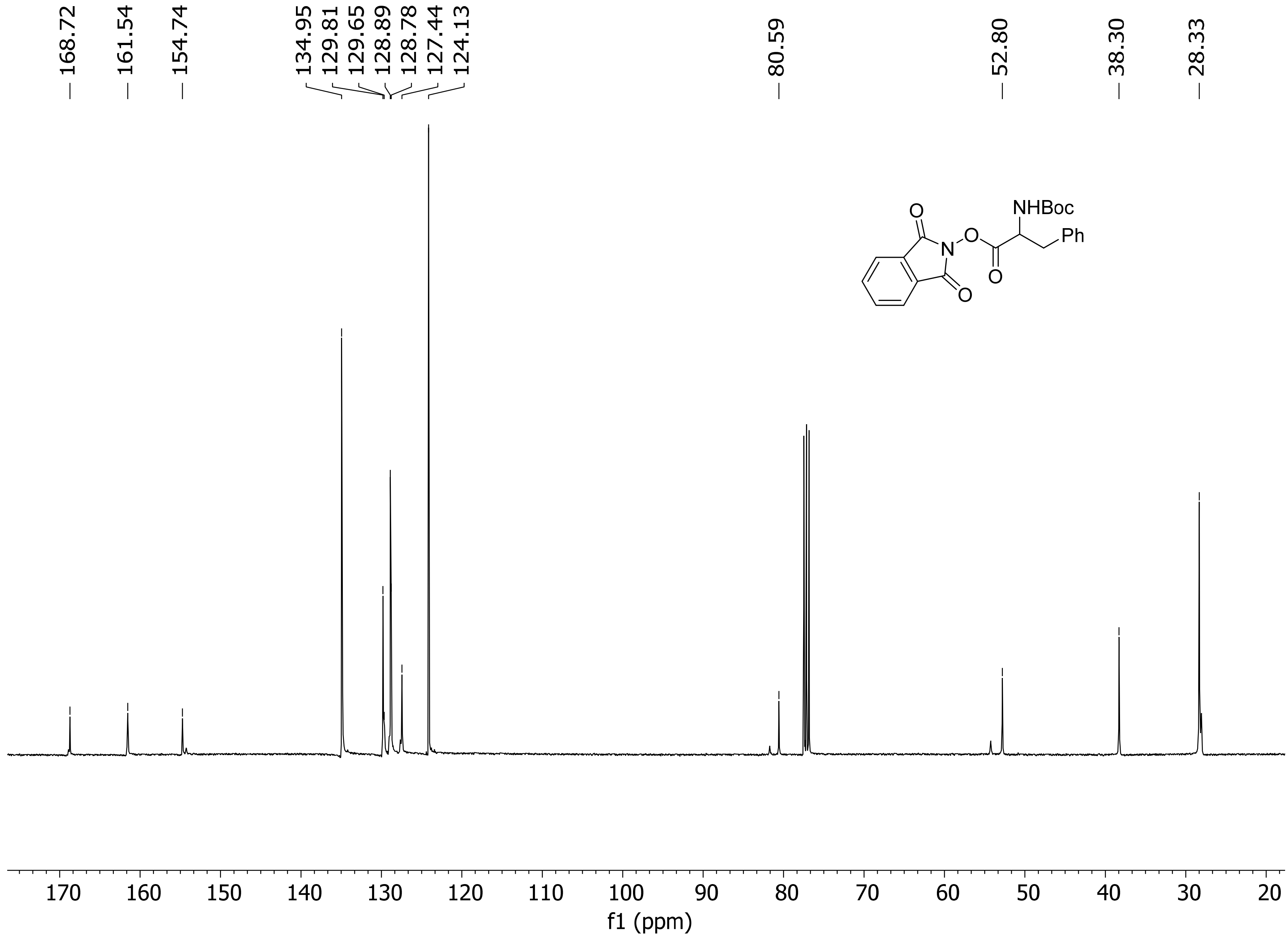

169.04
161.66
155.28
134.94
128.95
124.12
80.54
57.22
31.92
28.39
18.85
17.51
O
N
O
O
O
NHBoc
i-Pr
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

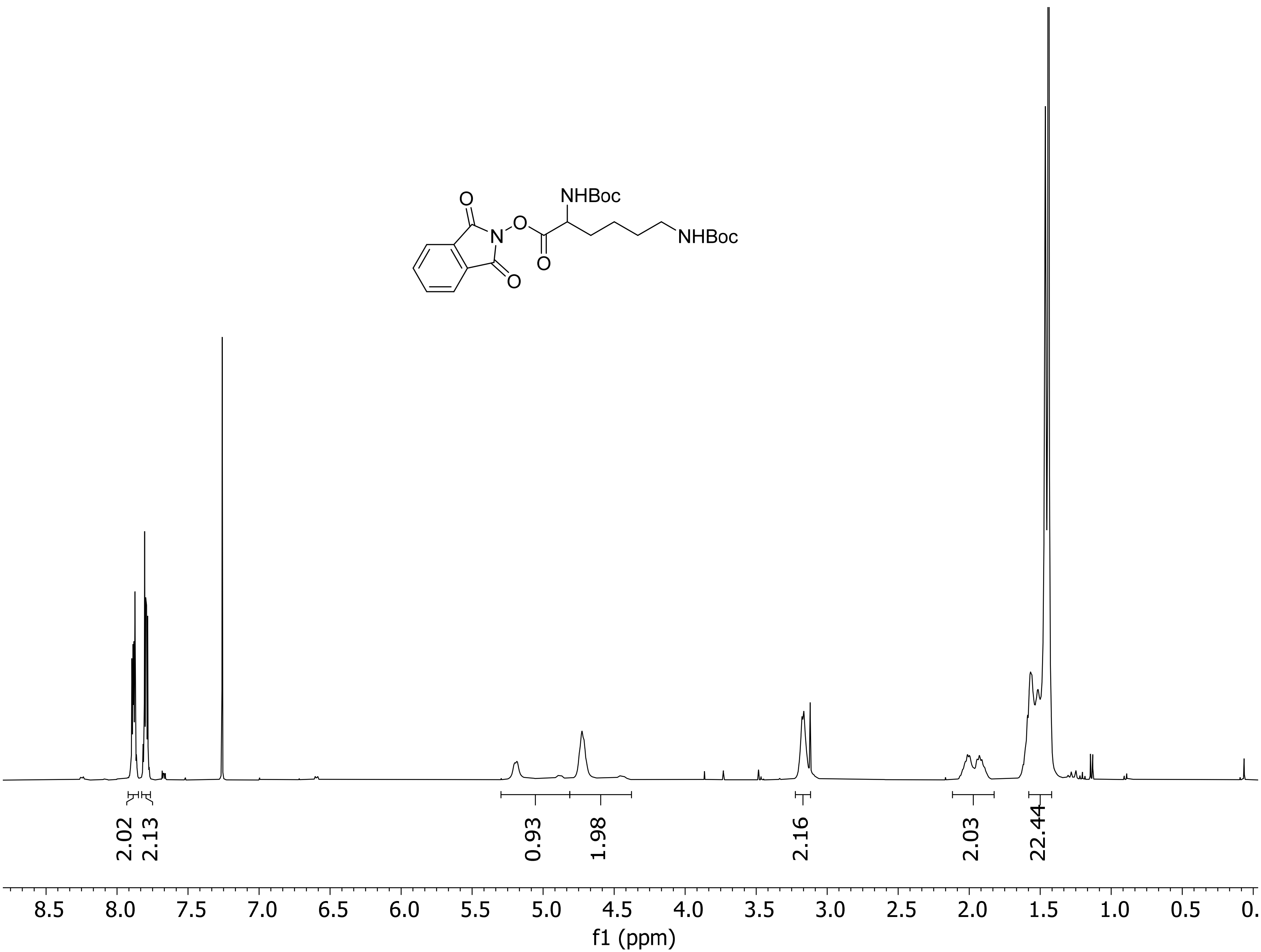

NHBoc
Ph
2.02
2.05
5.76
0.72
0.97
0.20
2.05
2.04
9.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


169.48
161.63
154.93
140.49
134.98
128.96
128.73
128.65
126.44
124.17
80.73
51.91
34.92
31.37
28.41
NHBoc
O
N
O
O
O
Ph
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

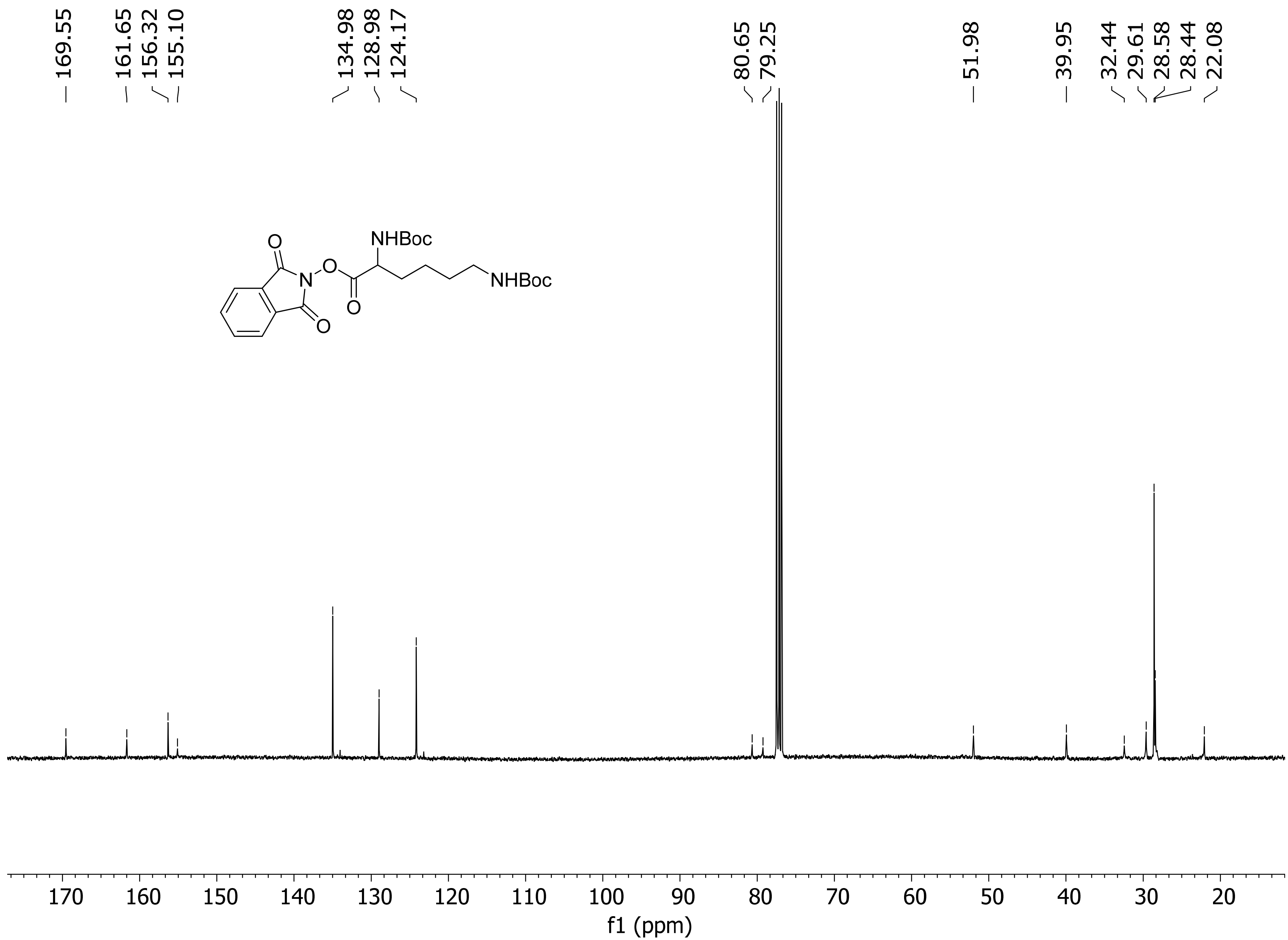


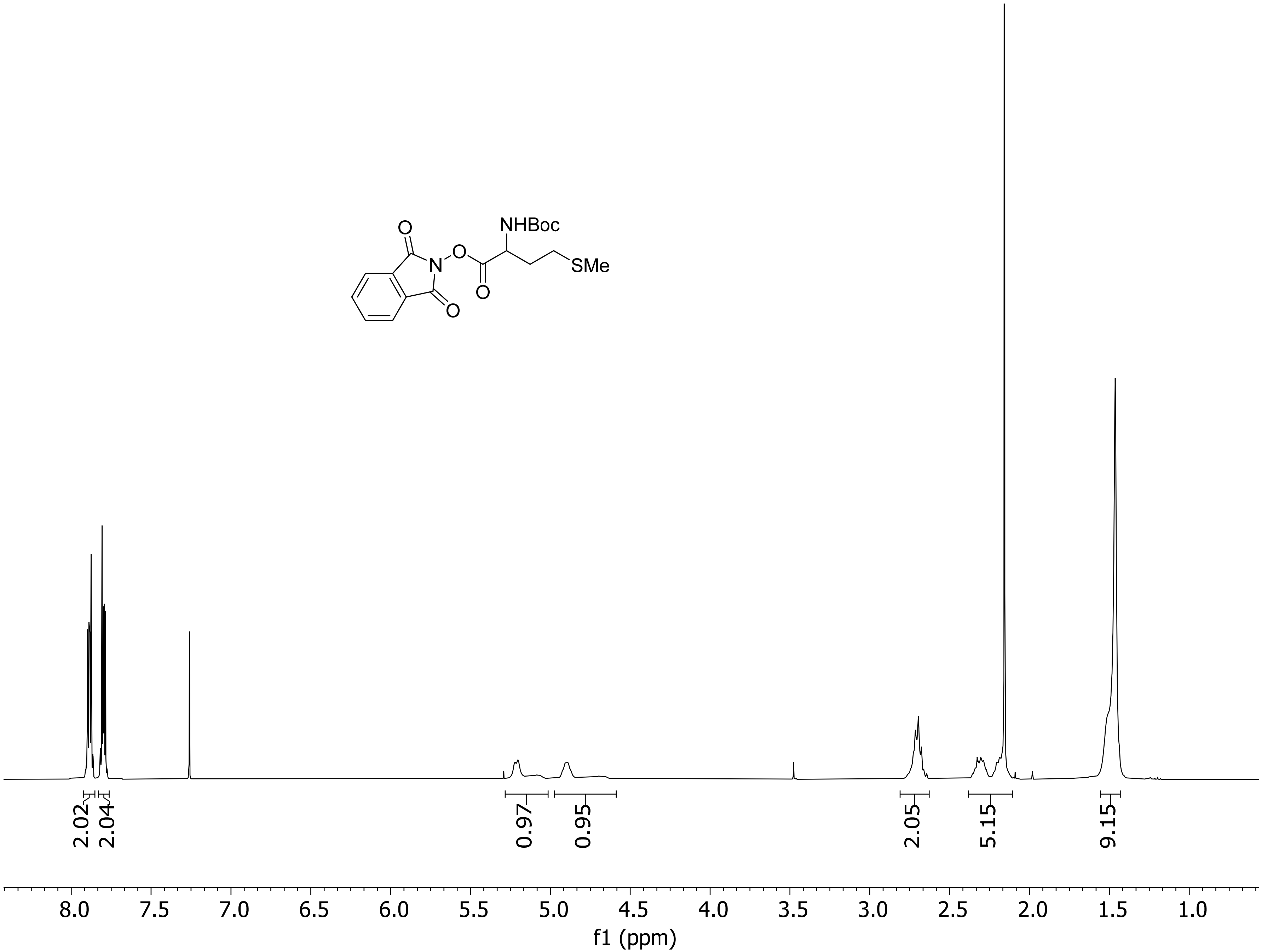
NHBoc
Ph
O
N
O
O
O
2.02
2.04
5.32
1.97
2.03
9.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

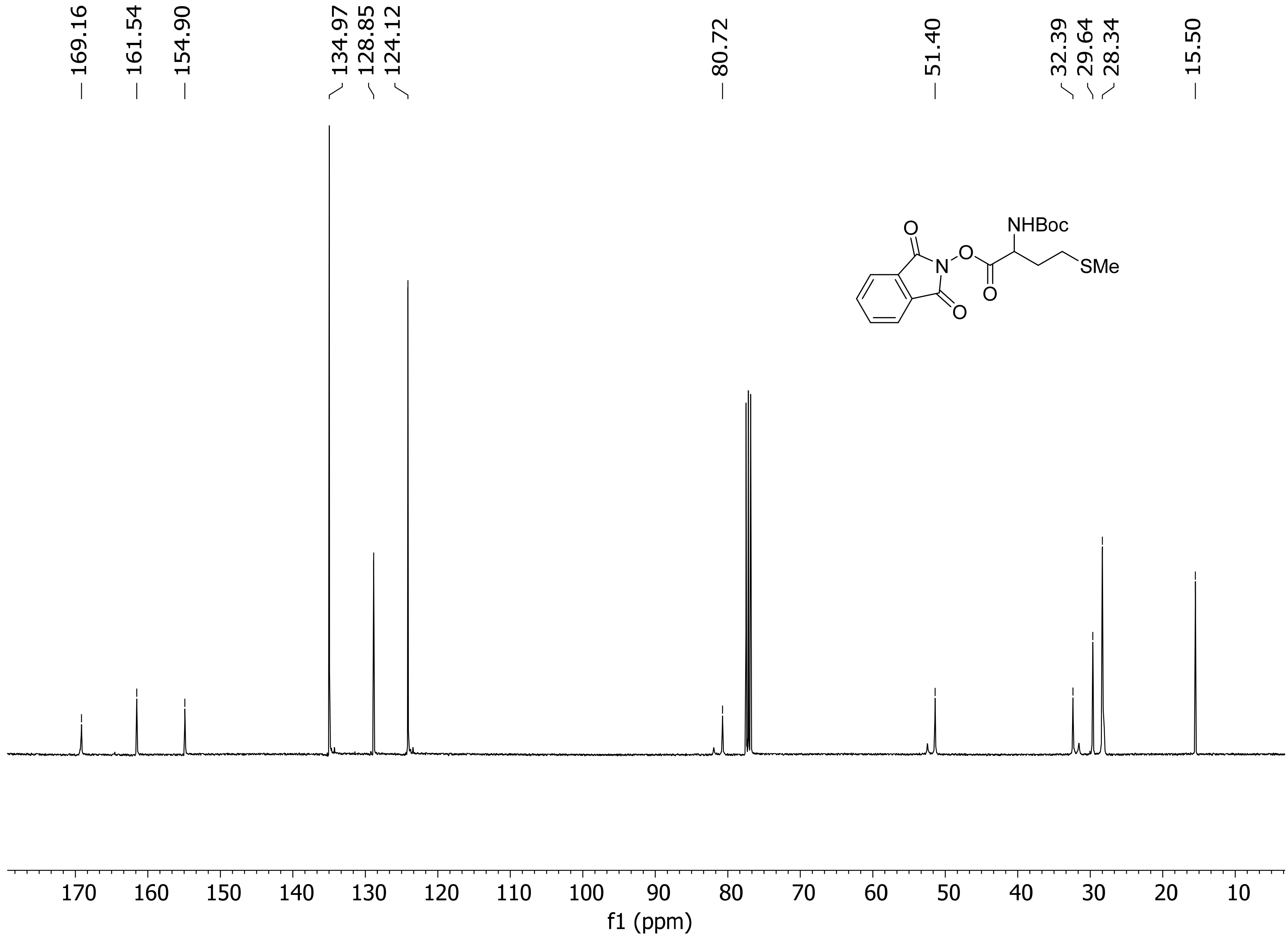

168.72
161.54
154.74
134.95
129.81
129.65
128.89
128.78
127.44
124.13
80.59
52.80
38.30
28.33
NHBoc
Ph
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



O
N
O
O
O
NHBoc
NHBoc
2.02
2.13
0.93
1.98
2.16
2.03
22.44
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


169.55
161.65
156.32
155.10
134.98
128.98
124.17
80.65
79.25
51.98
39.95
32.44
29.61
28.58
28.44
22.08
NHBoc
NHBoc
O
N
O
O
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


NHBoc
SMe
O
N
2.02
2.04
0.97
0.95
2.05
5.15
9.15
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)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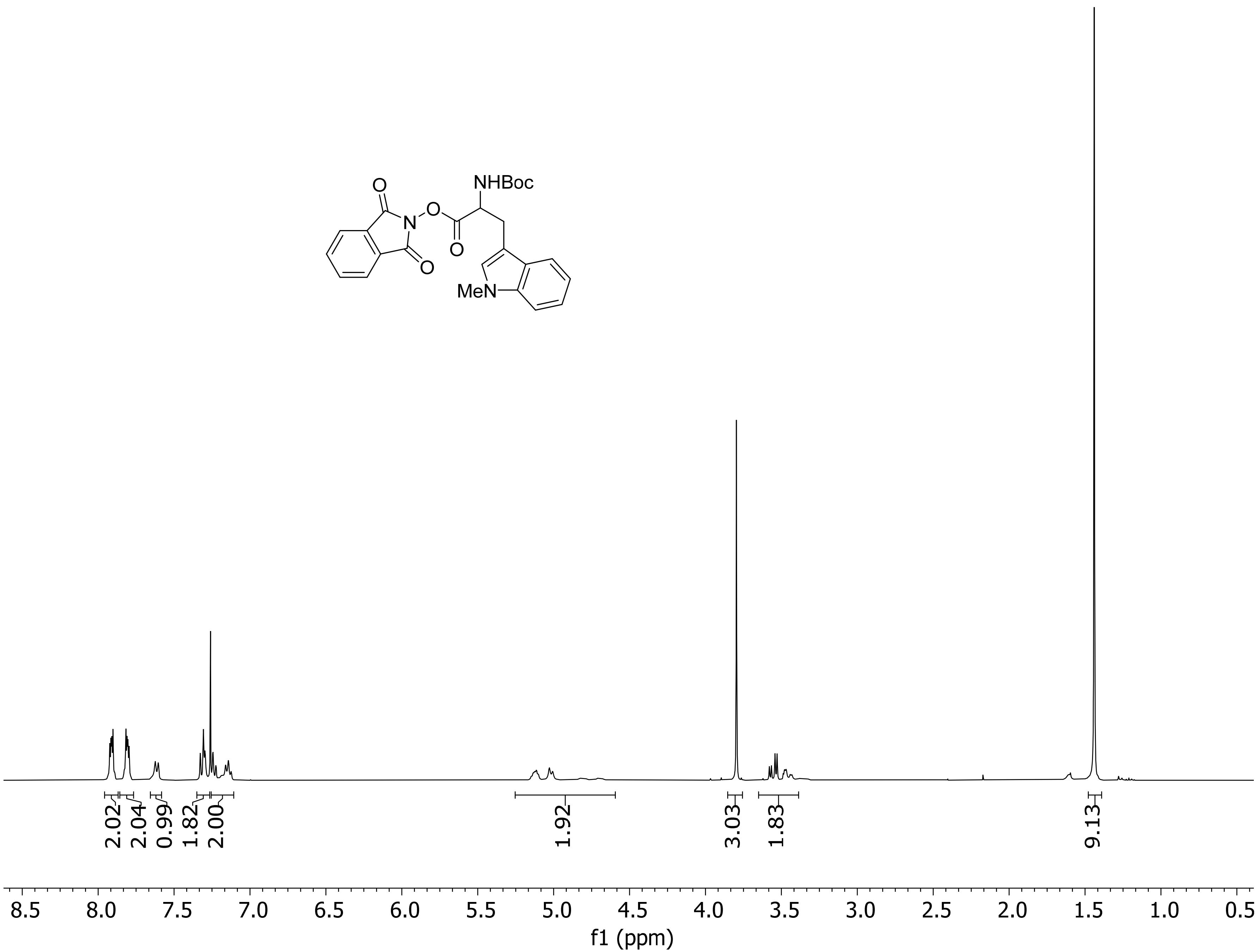
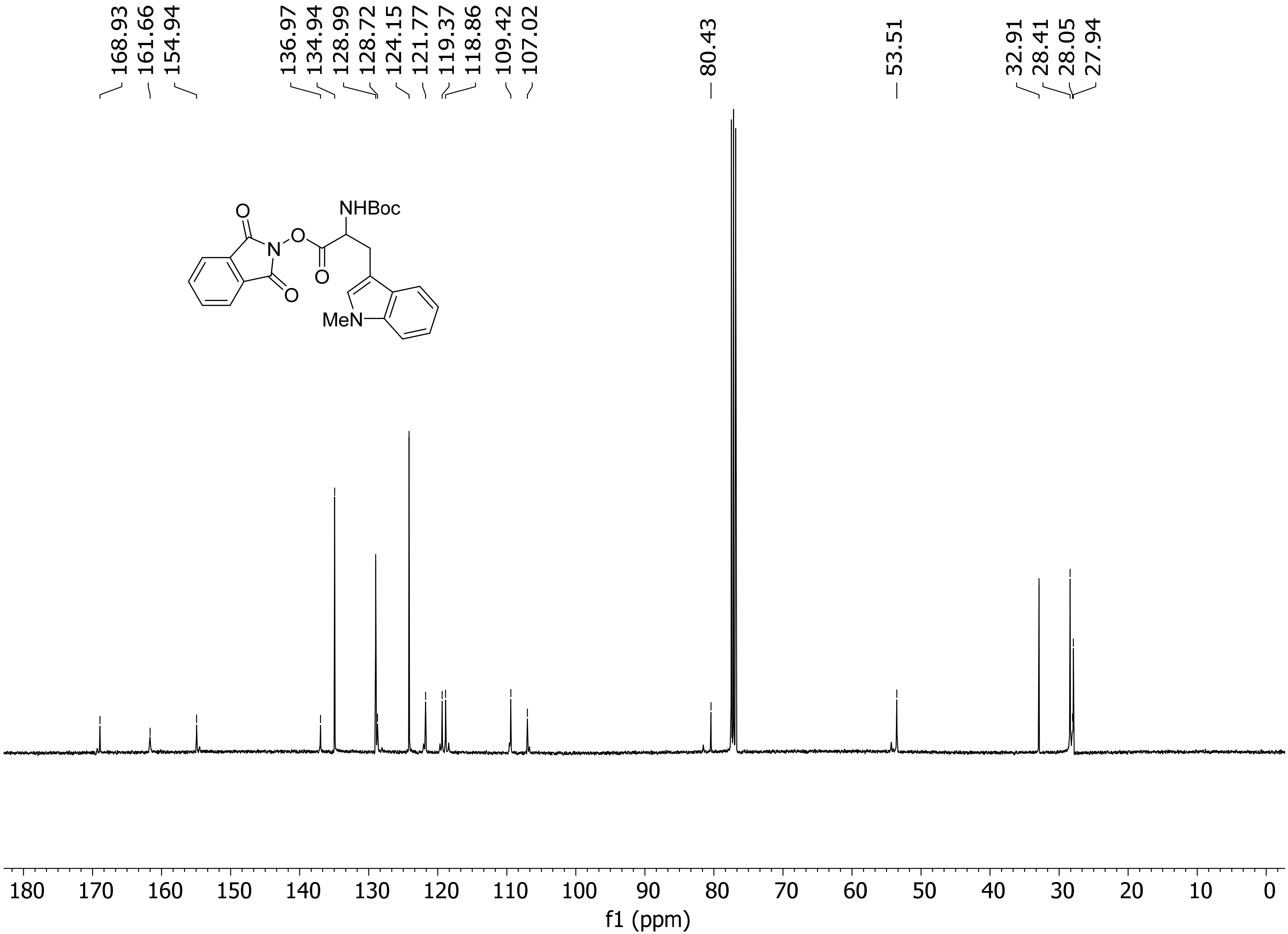
161.54
154.90
134.97
128.85
124.12
80.72
51.40
32.39
29.64
28.34
15.50
NHBoc
SMe
O
N
f1 (ppm)


NHBoc
MeN
2.02
2.04
0.99
1.82
2.00
1.92
3.03
1.83
9.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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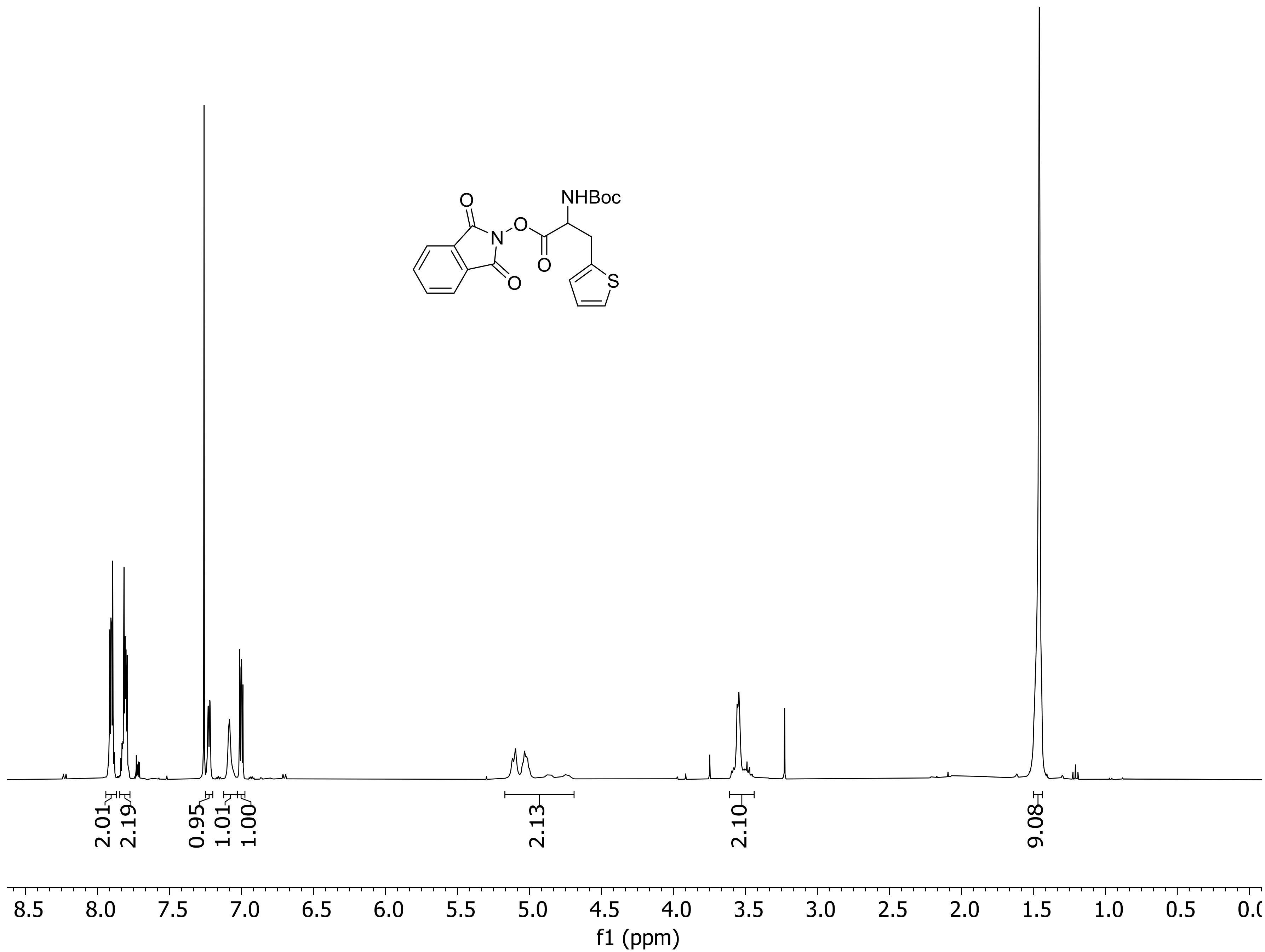
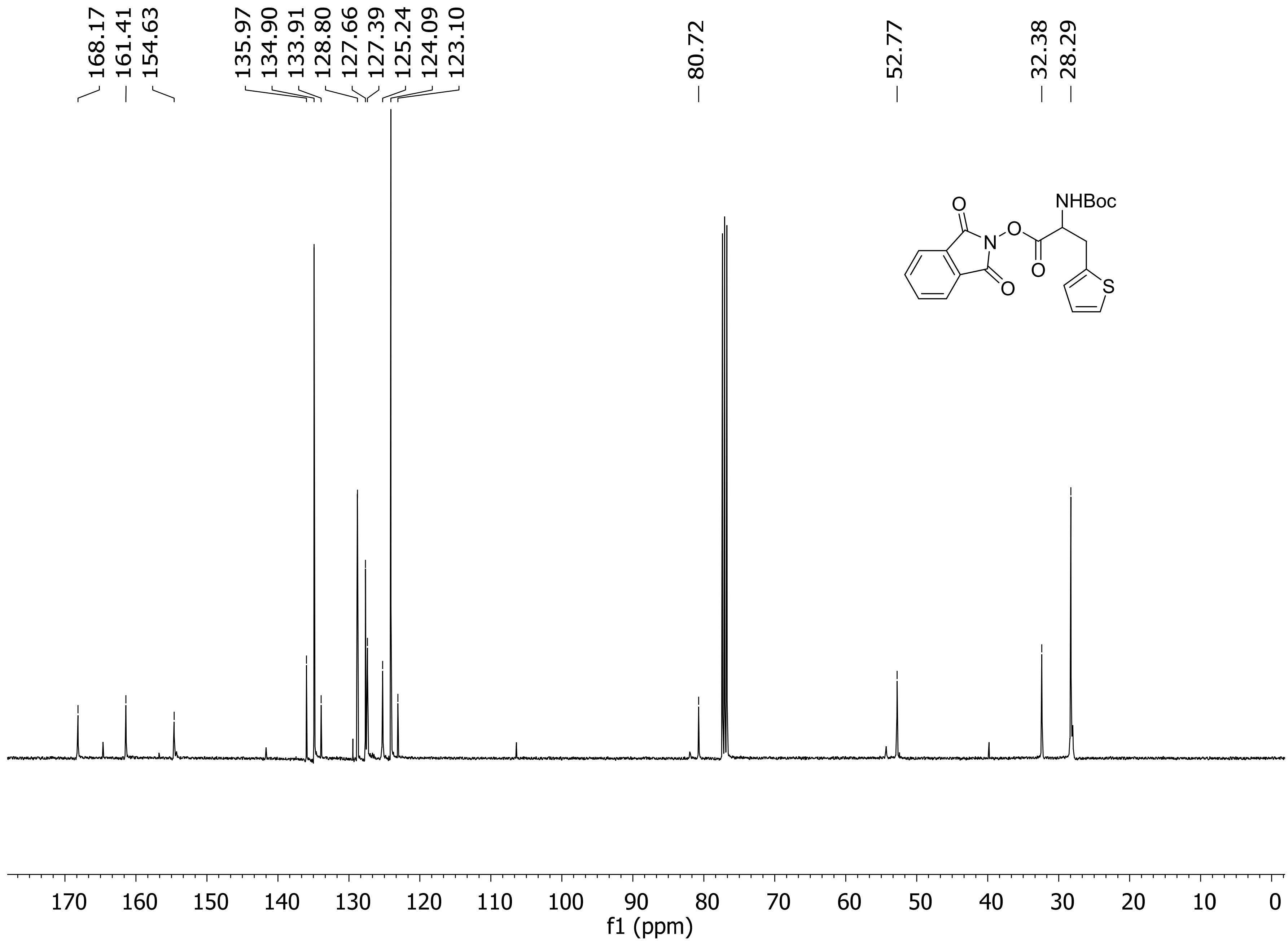
134.94
128.99
128.72
124.15
121.77
119.37
118.86
109.42
107.02
80.43
53.51
32.91
28.41
28.05
27.94
NHBoc
MeN
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NHBoc
O
N
O
O
O
S
2.01
2.19
0.95
1.01
1.00
2.13
2.10
9.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



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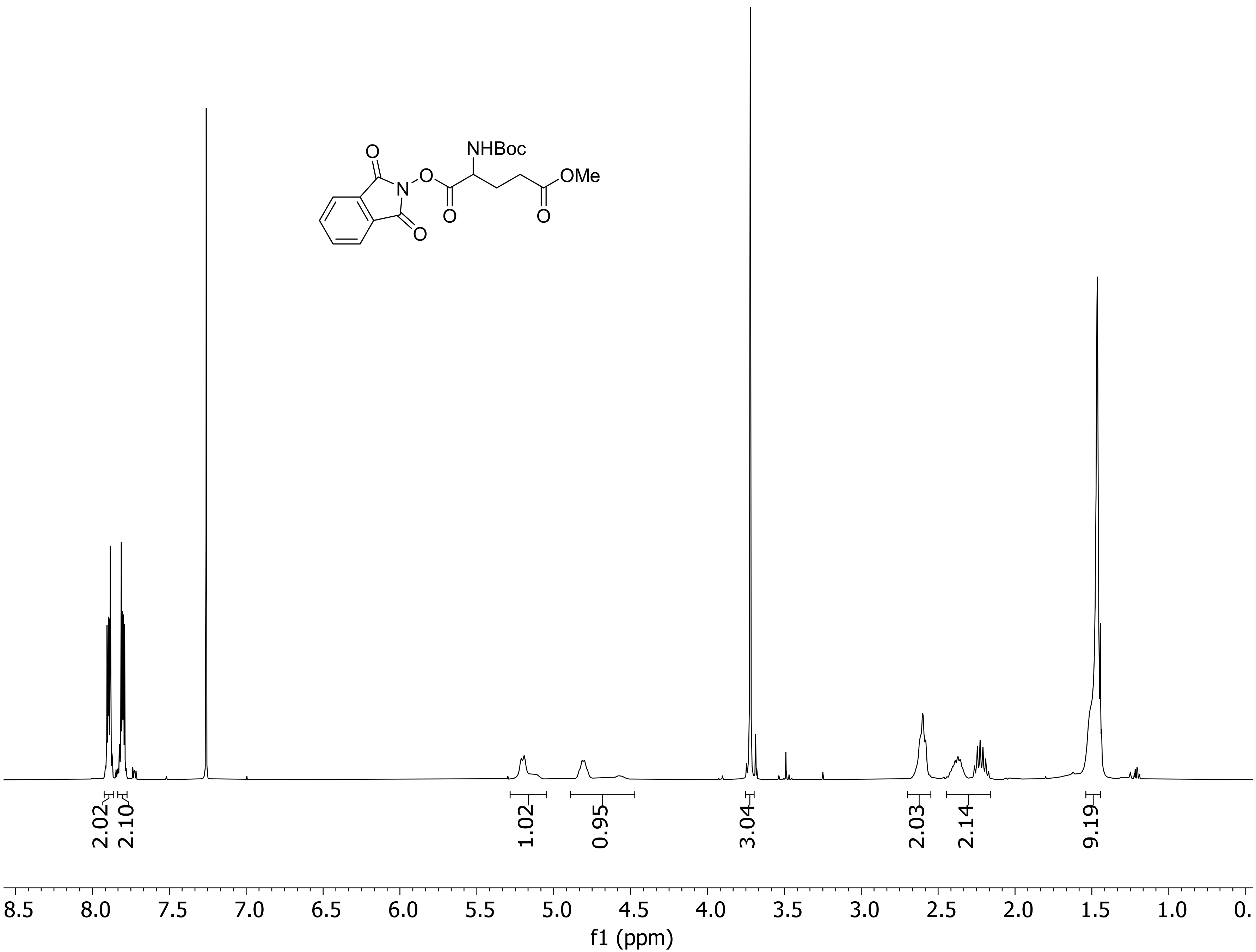
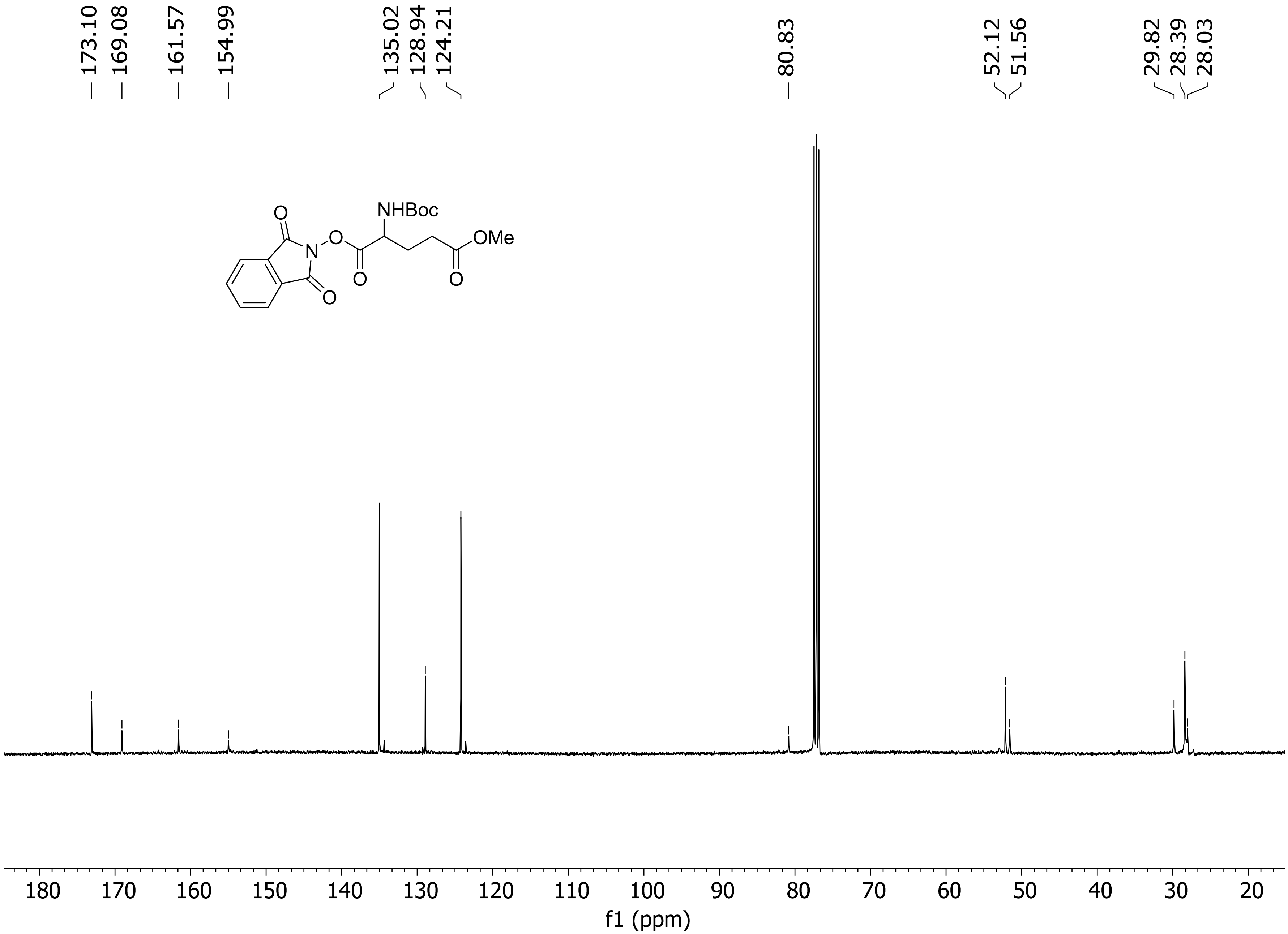
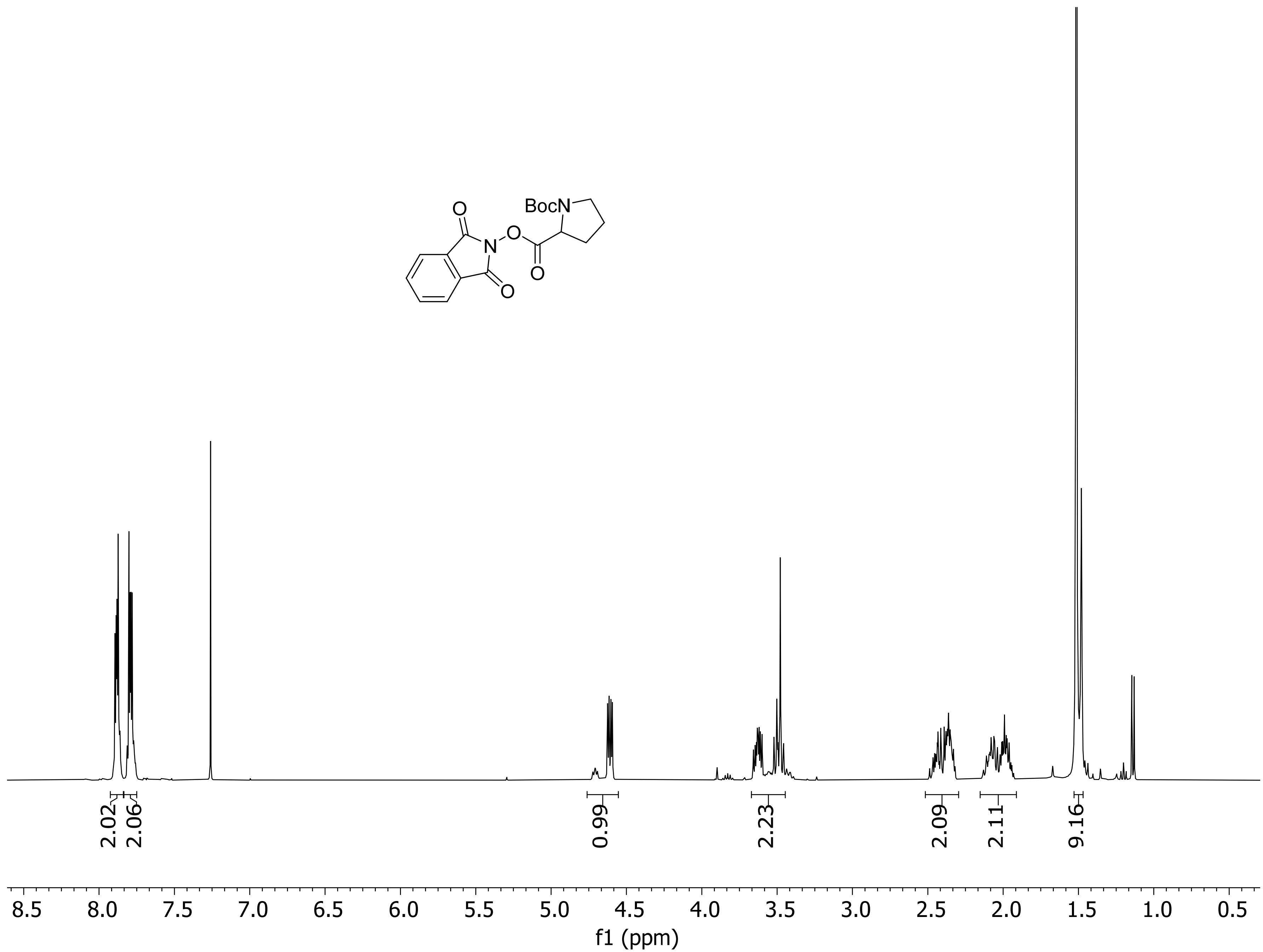
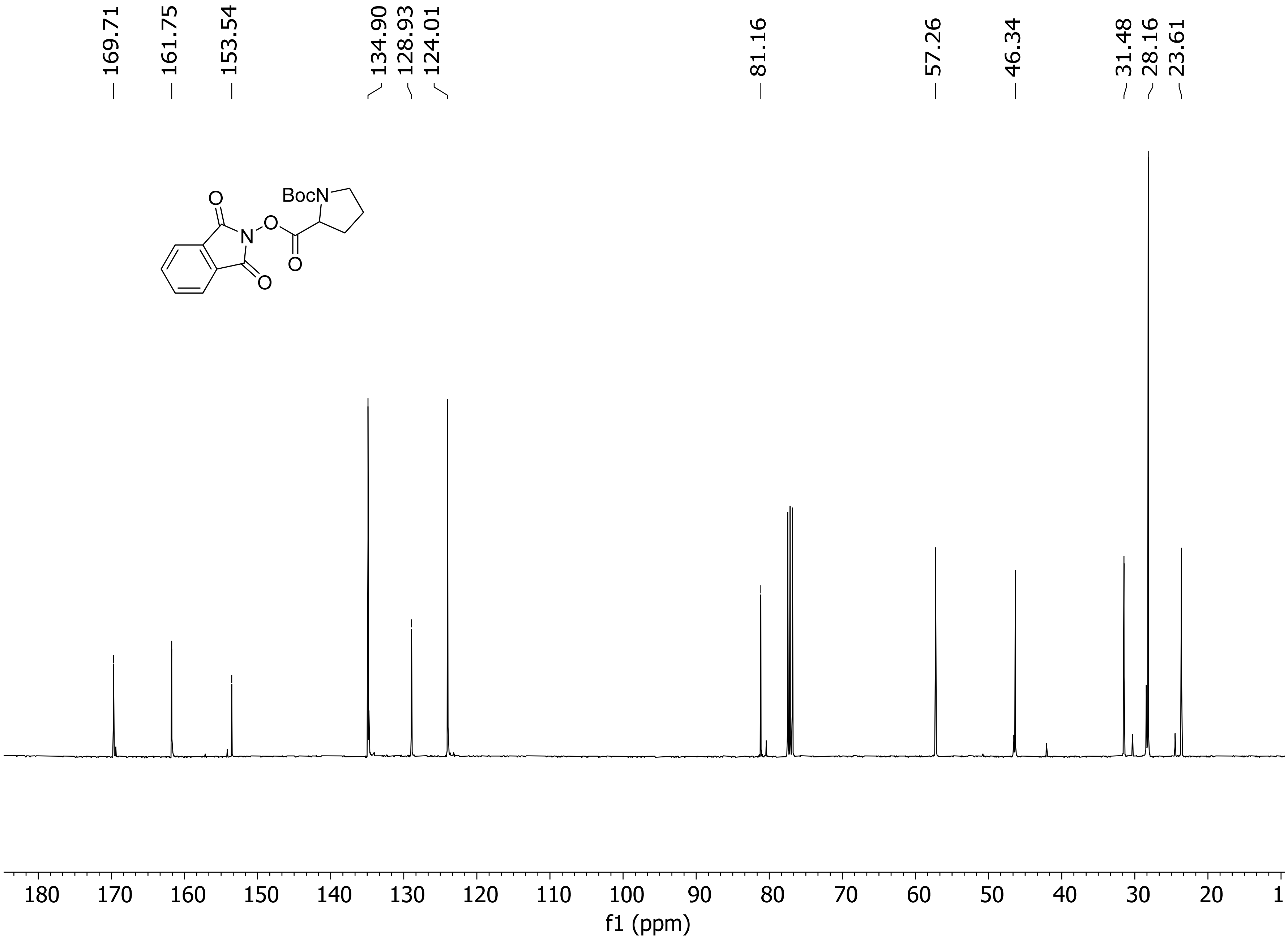
161.41
154.63
135.97
134.90
133.91
128.80
127.66
127.39
125.24
124.09
123.10
80.72
52.77
32.38
28.29
NHBoc
O
N
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



NHBoc
OMe
2.02
2.10
1.02
0.95
3.04
2.03
2.14
9.19
f1 (ppm)


173.10
169.08
161.57
154.99
135.02
128.94
124.21
80.83
52.12
51.56
29.82
28.39
28.03
NHBoc
OMe
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


BocN
O
N
O
O
O
2.02
2.06
0.99
2.23
2.09
2.11
9.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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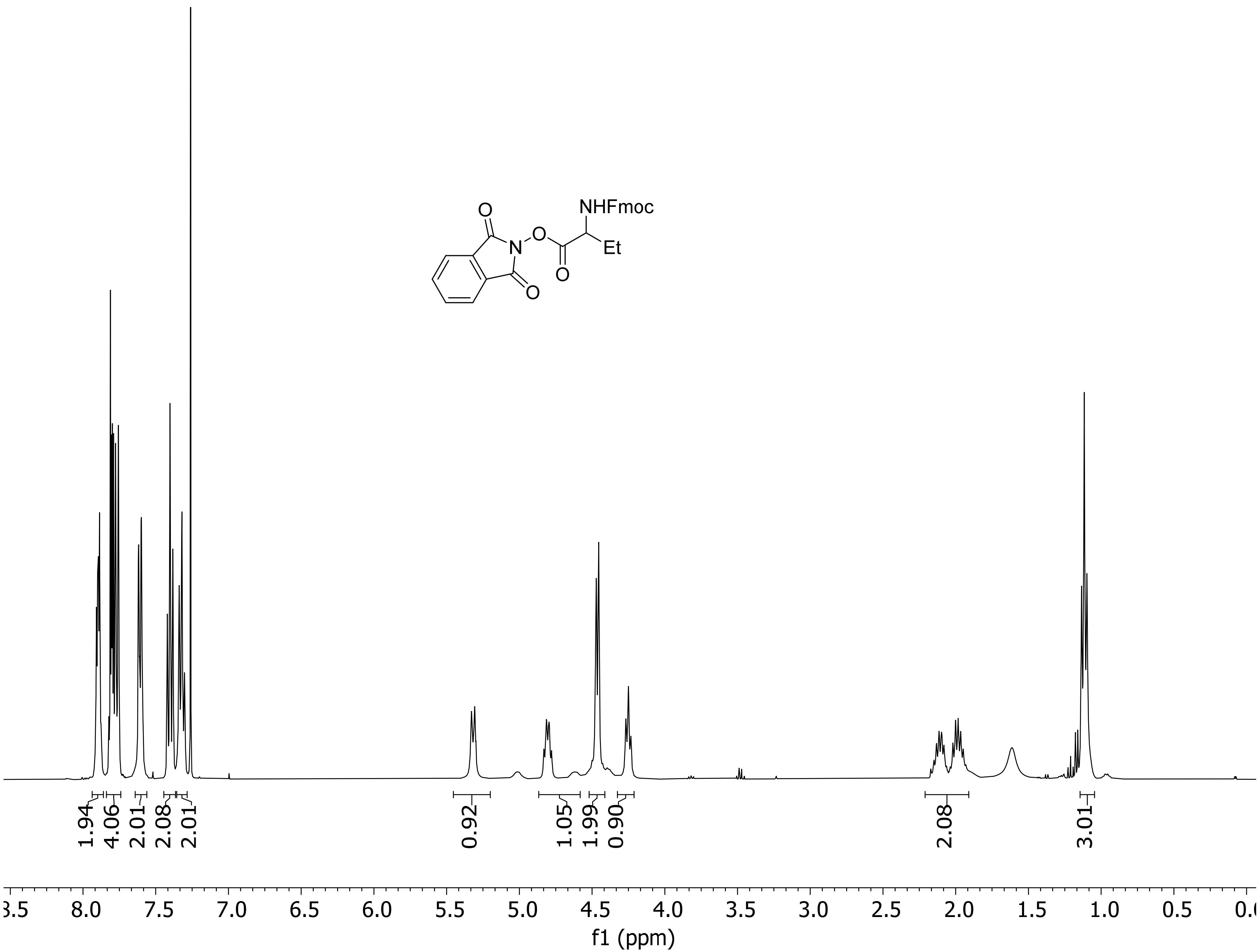
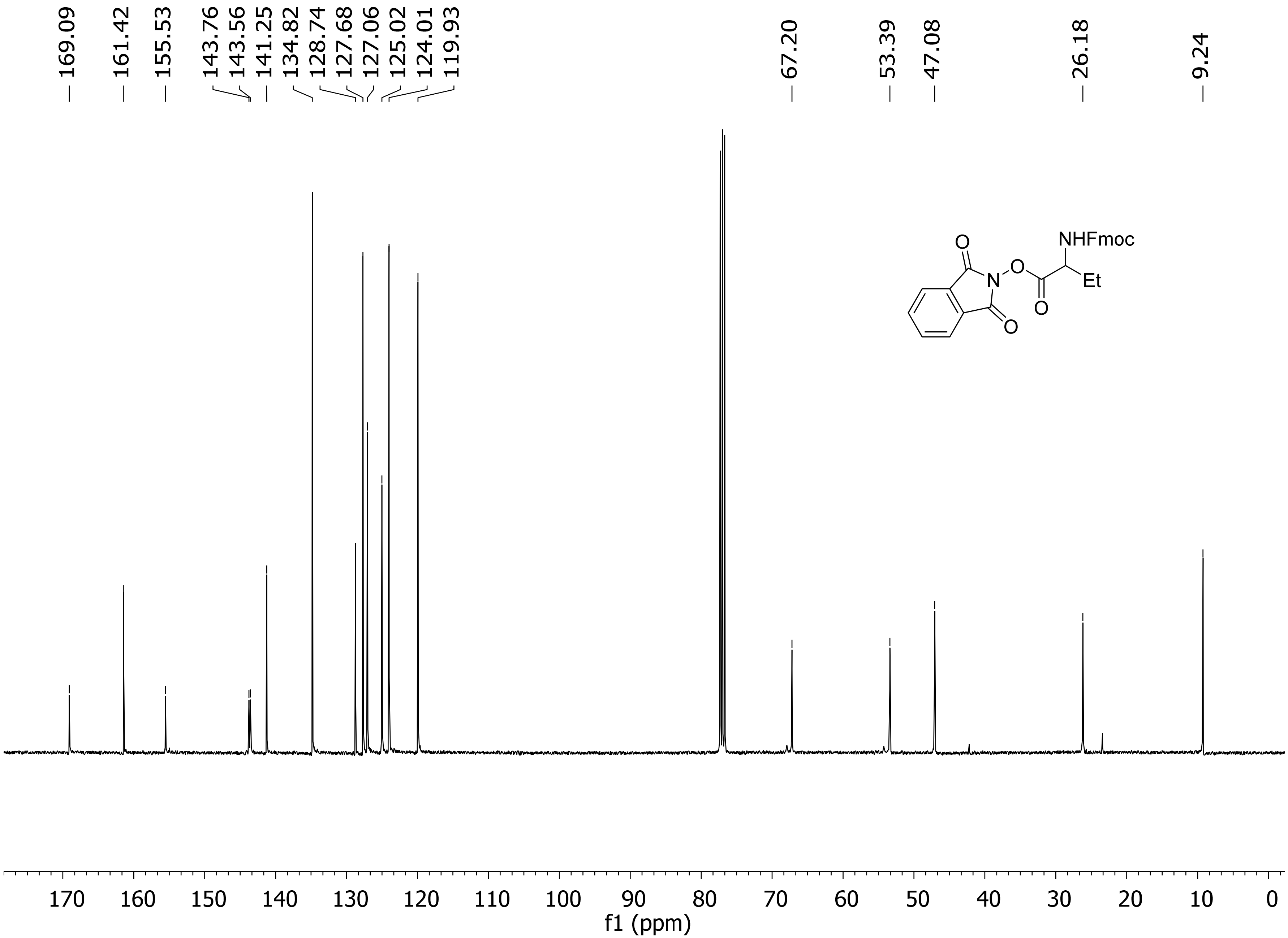
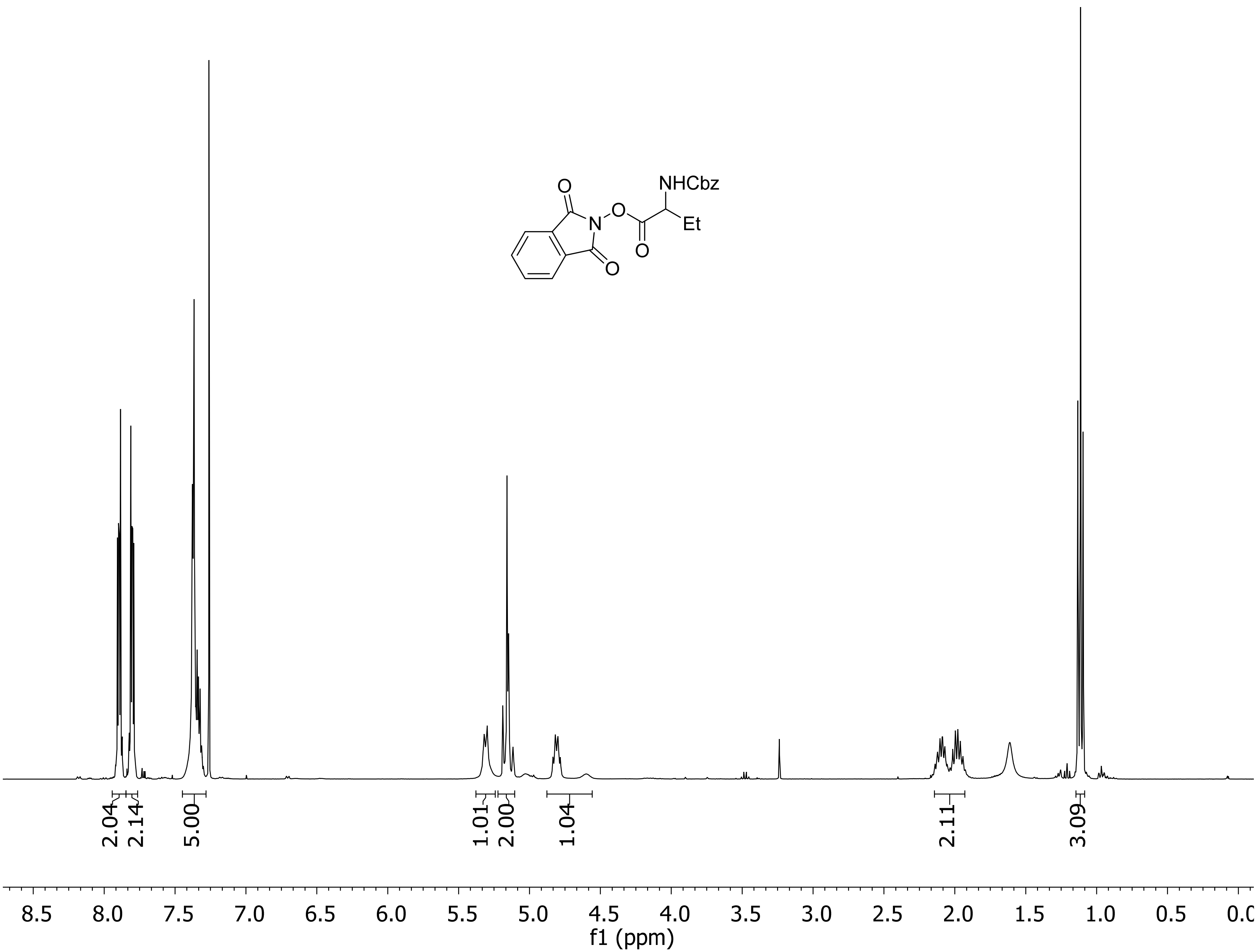
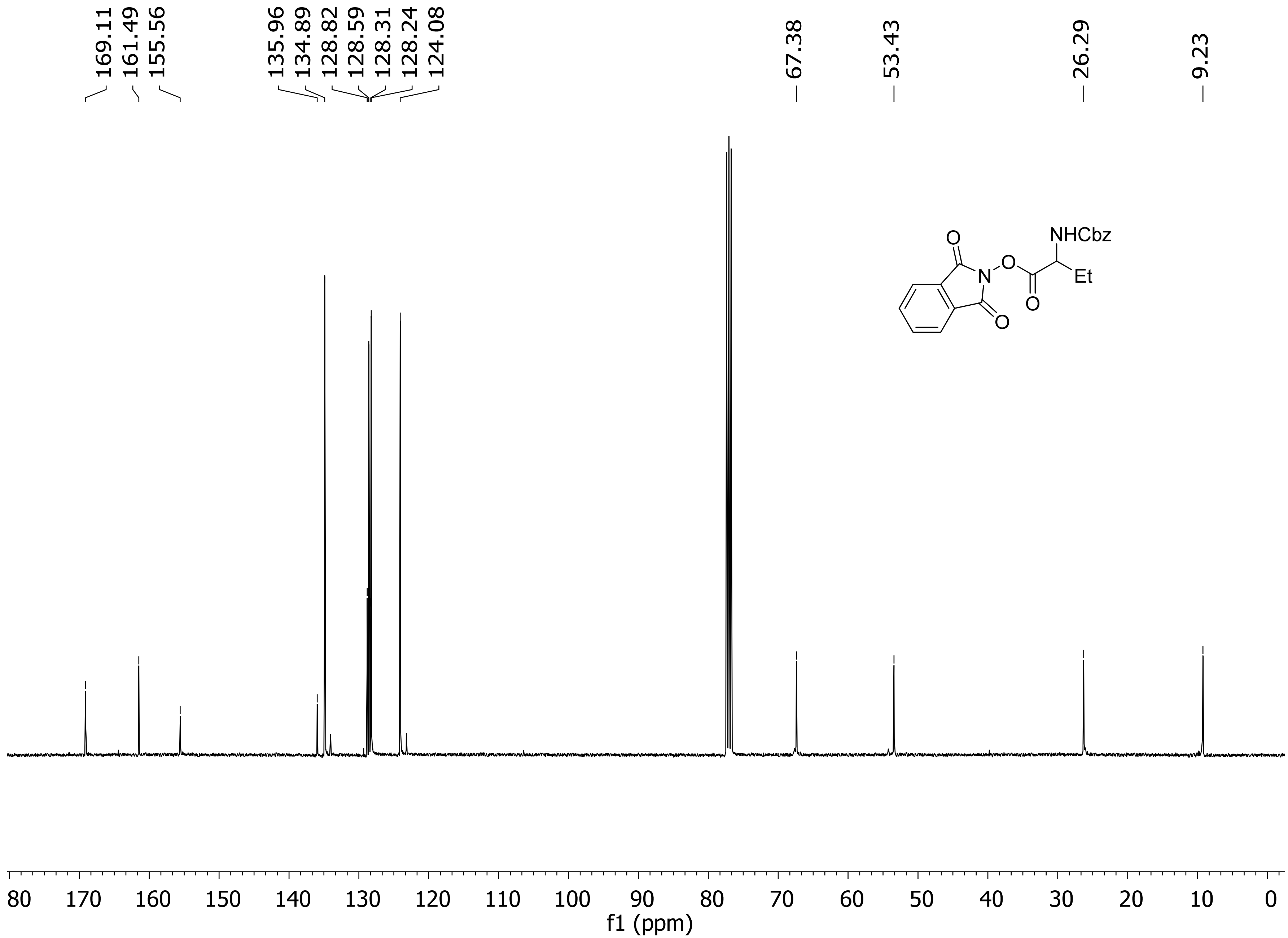
161.75
153.54
134.90
128.93
124.01
81.16
57.26
46.34
31.48
28.16
23.61
BocN
O
N
O
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 1
f1 (ppm)



O
N
O
O
O
NHFmoc
Et
O
1.94
4.06
2.01
2.08
2.01
0.92
1.05
1.99
0.90
2.08
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


169.09
161.42
155.53
143.76
143.56
141.25
134.82
128.74
127.68
127.06
125.02
124.01
119.93
67.20
53.39
47.08
26.18
9.24
NHFmoc
Et
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
O
O
O
NHCbz
Et
2.04
2.14
5.00
1.01
2.00
1.04
2.11
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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155.56
135.96
134.89
128.82
128.59
128.31
128.24
124.08
67.38
53.43
26.29
9.23
NHCbz
Et
O
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

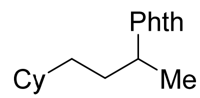
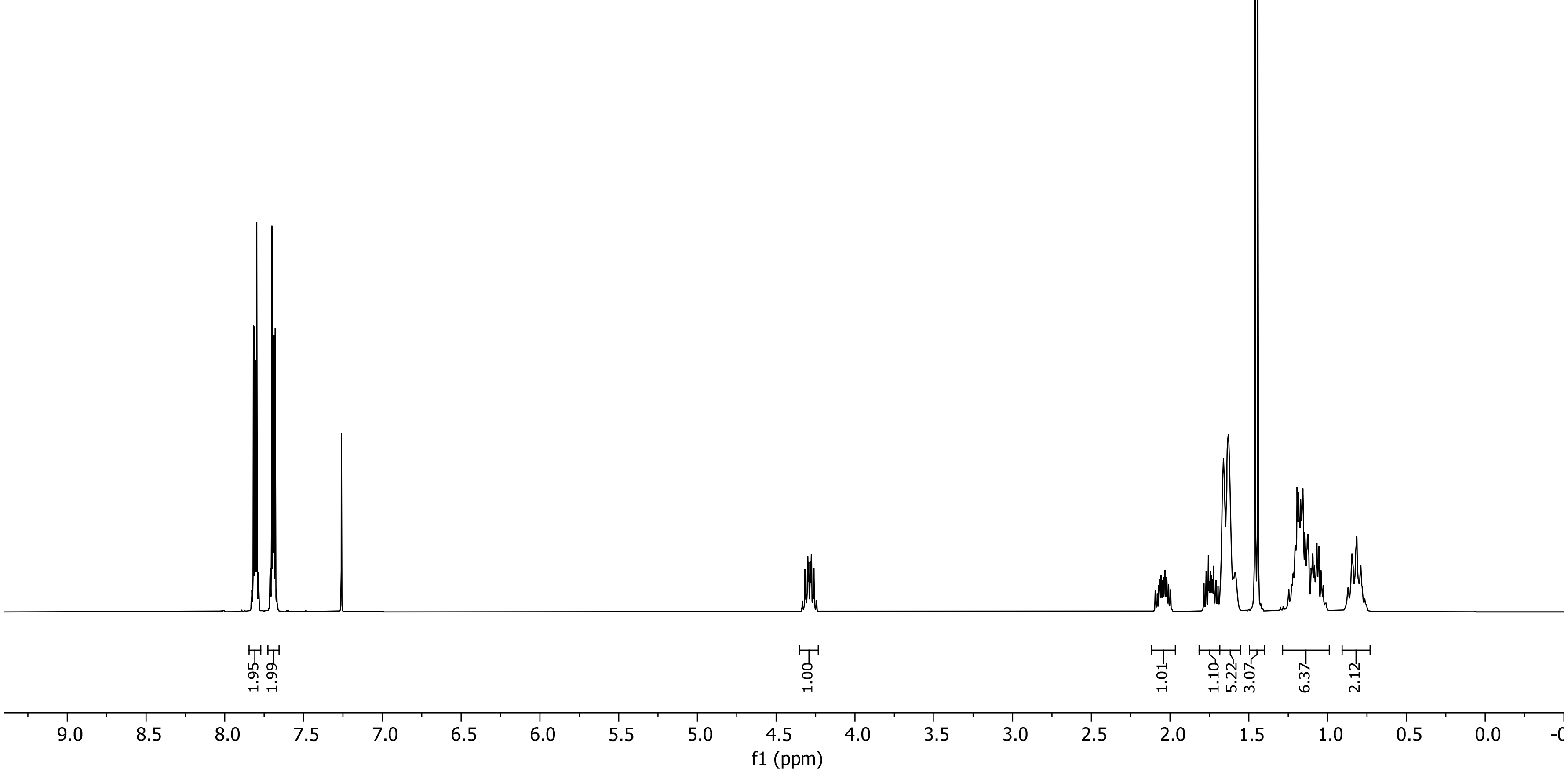
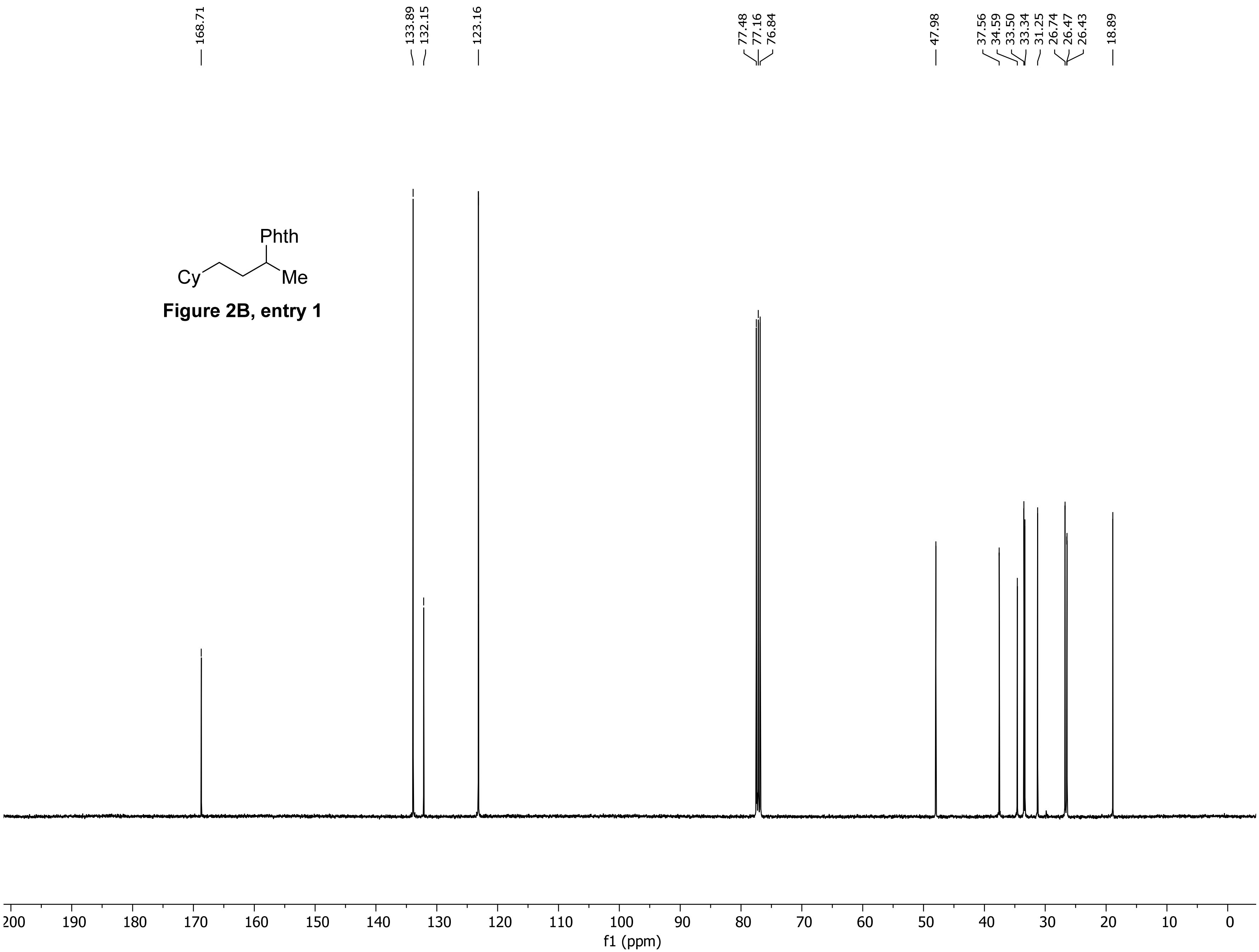


Figure 2B, entry 1




168.71
133.89
132.15
123.16
77.48
77.16
76.84
47.98
37.56
34.59
33.50
33.34
31.25
26.74
26.47
26.43
18.89
Phth
Cy
Me
Figure 2B, entry 1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

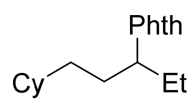
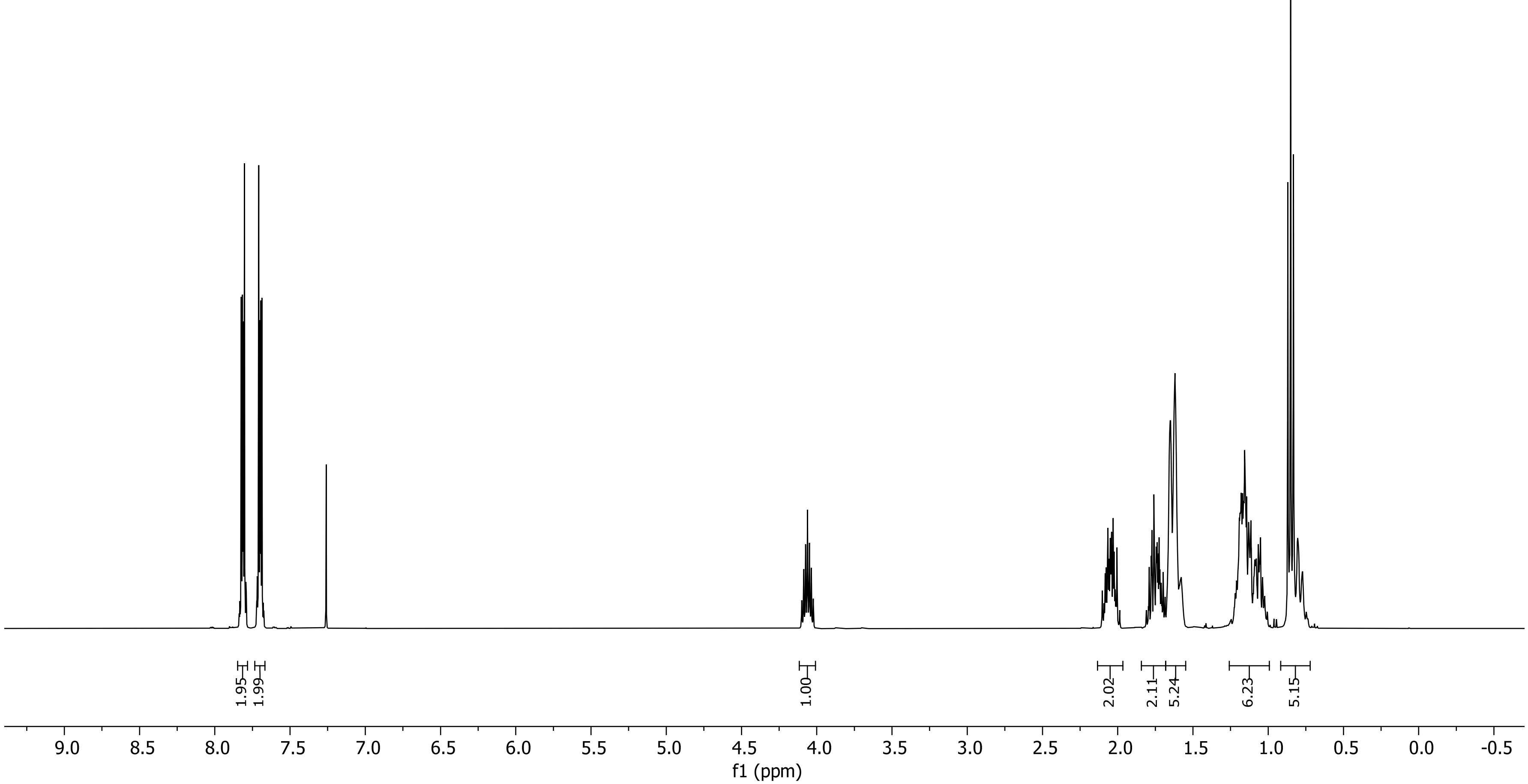
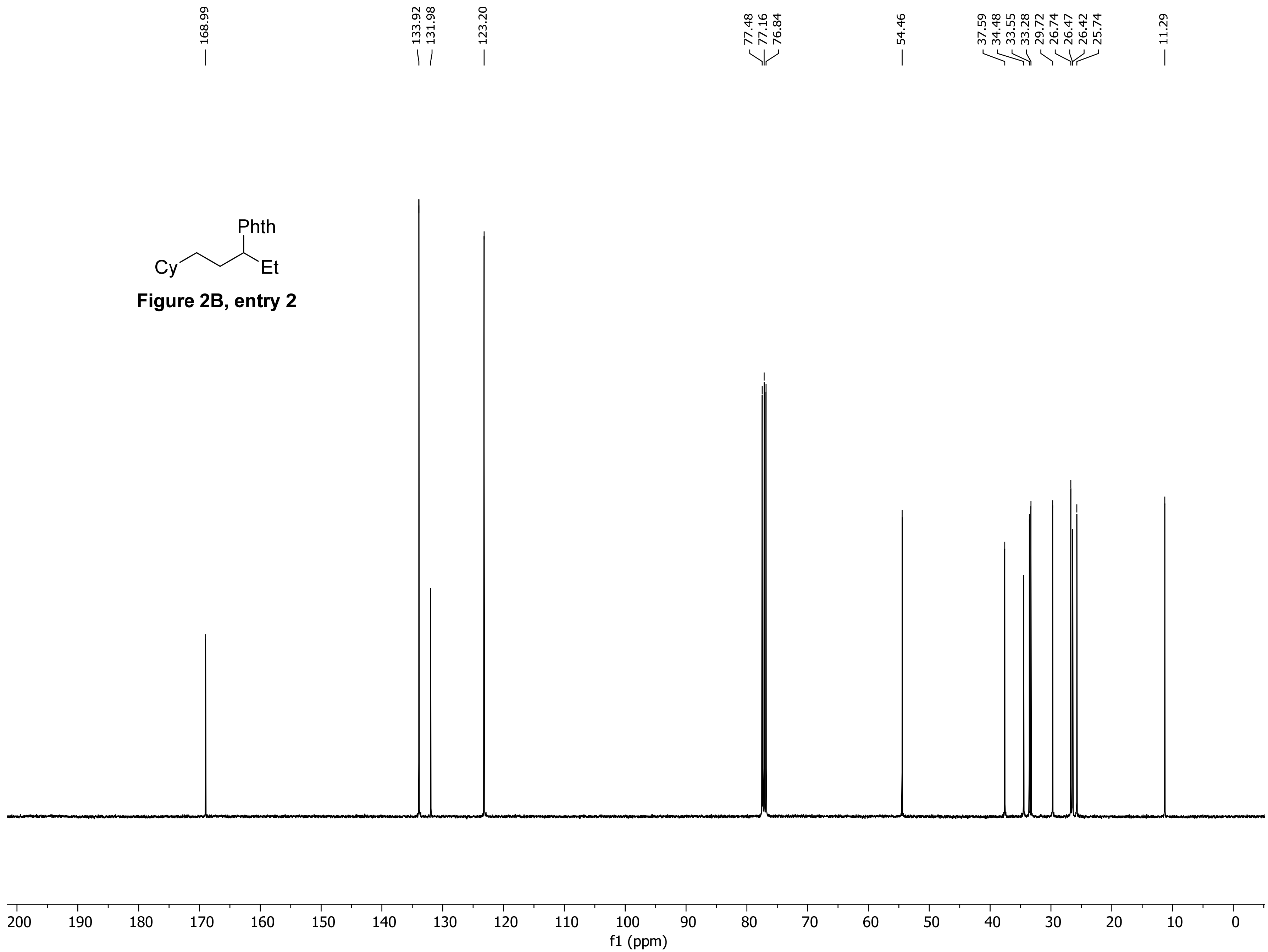


Figure 2B, entry 2




168.99
133.92
131.98
123.20
77.48
77.16
76.84
54.46
37.59
34.48
33.55
33.28
29.72
26.74
26.47
26.42
25.74
11.29
Phth
Cy
Et
Figure 2B, entry 2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

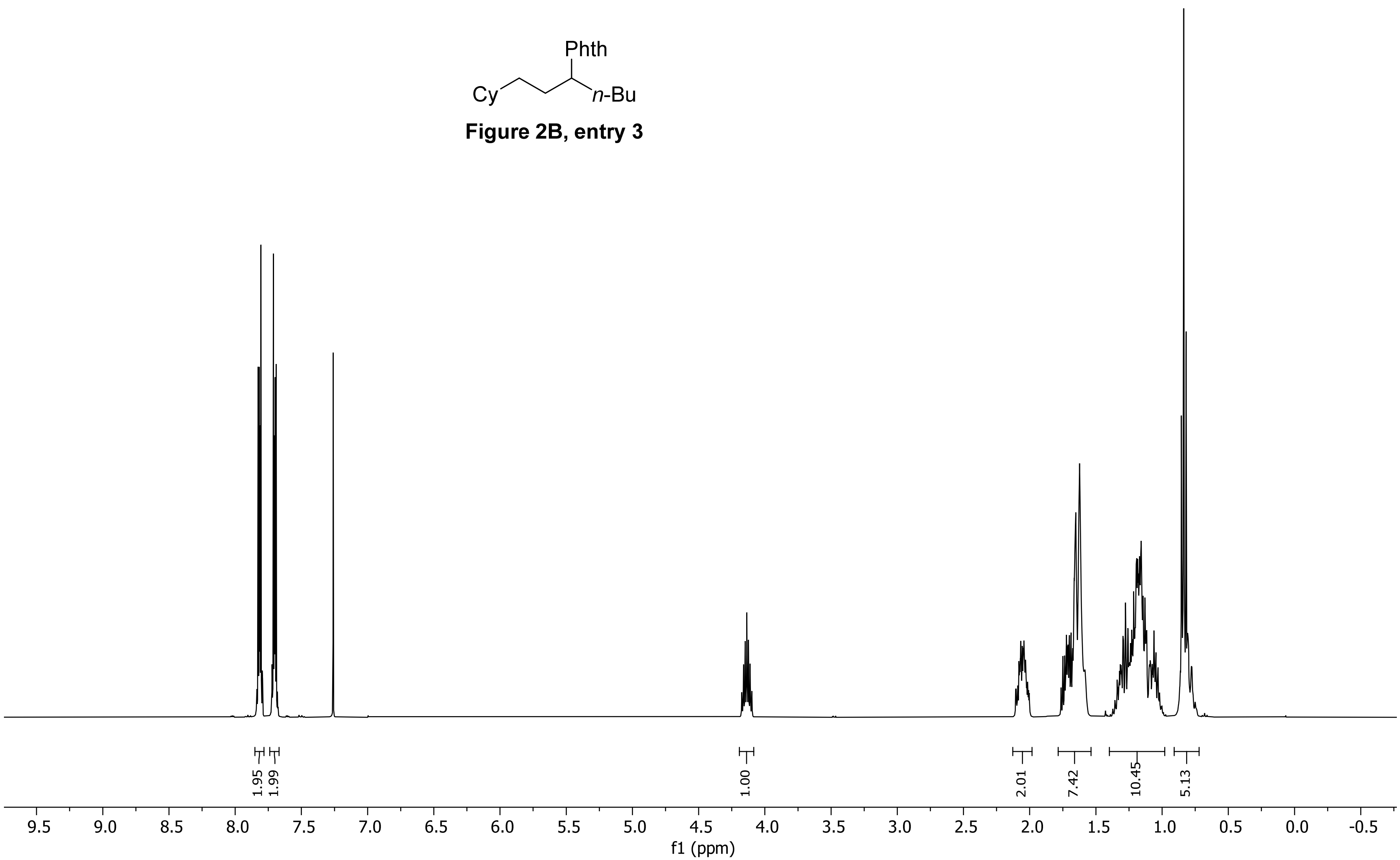


Figure 2B, entry 3

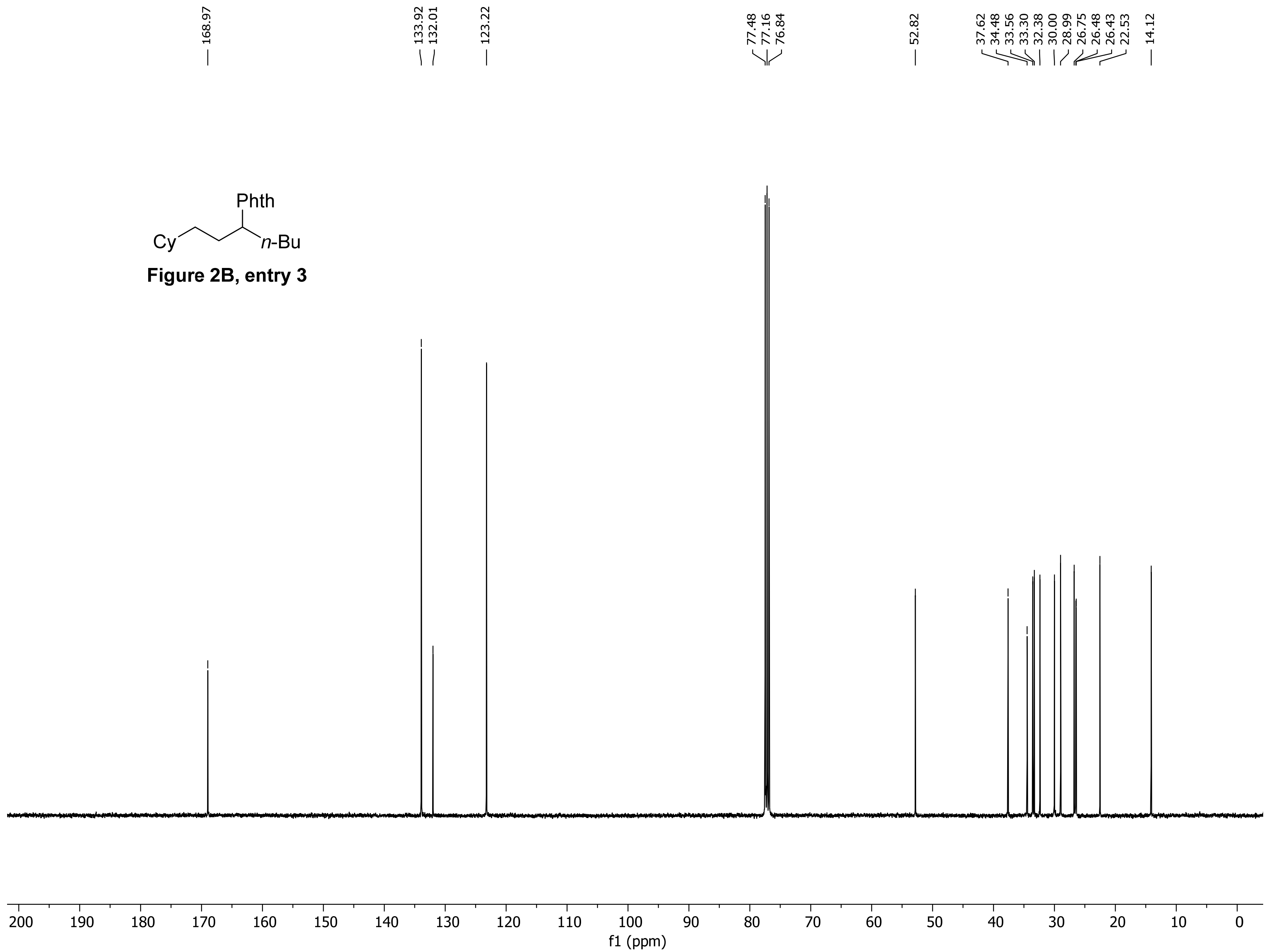


Figure 2B, entry 3

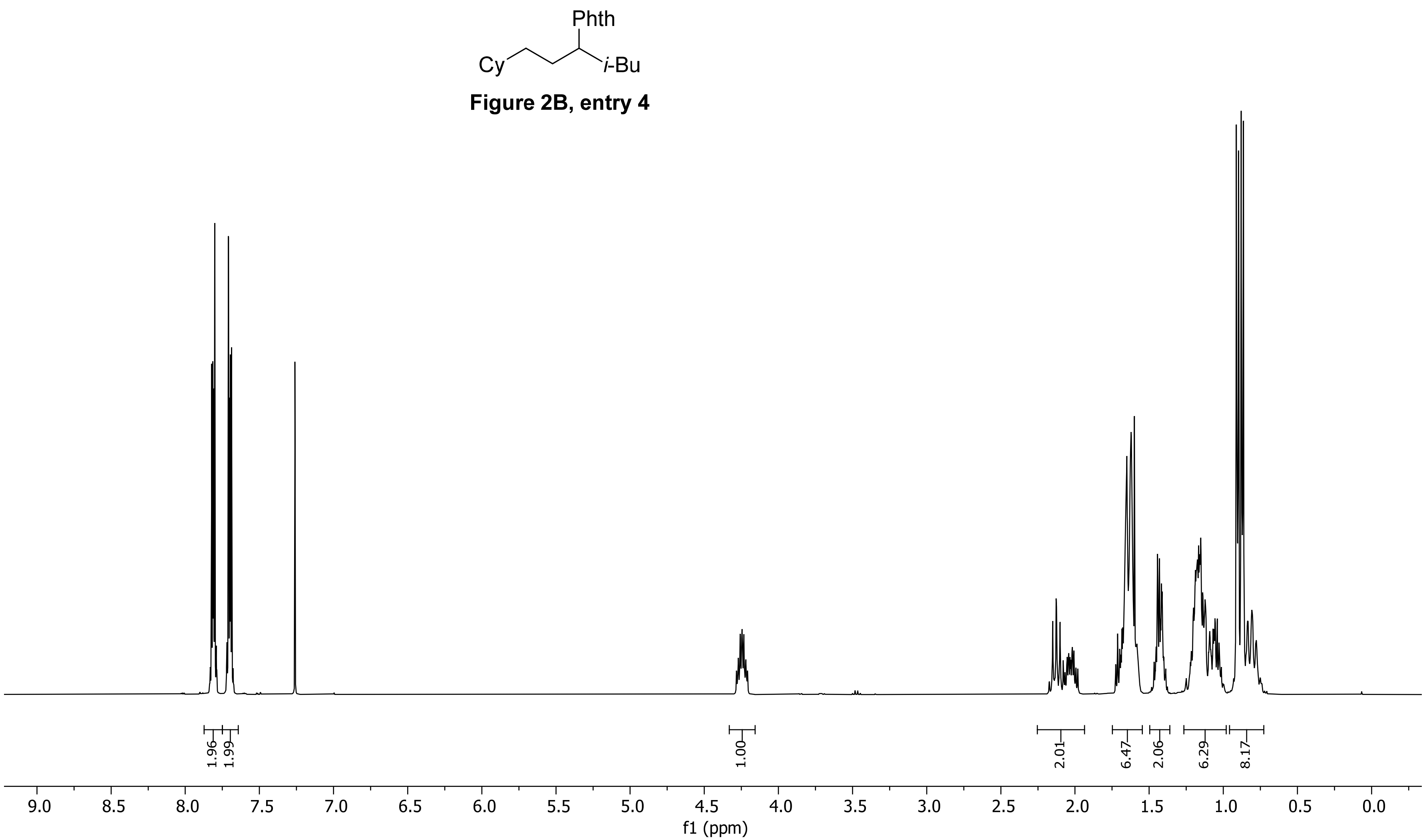
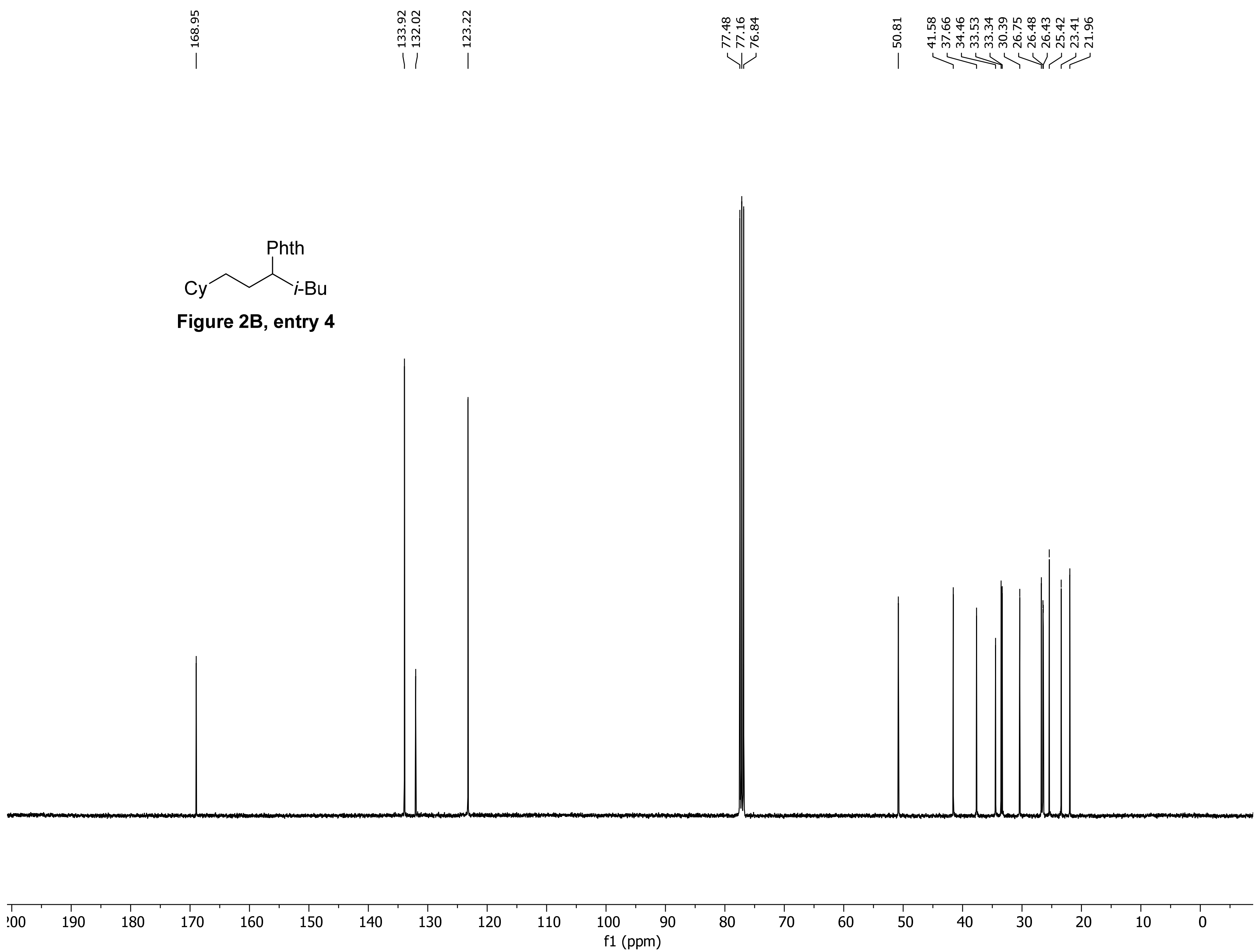


Figure 2B, entry 4


168.95
133.92
132.02
123.22
77.48
77.16
76.84
50.81
41.58
37.66
34.46
33.53
33.34
30.39
26.75
26.48
26.43
25.42
23.41
21.96
Phth
Cy
i-Bu
Figure 2B, entry 4
f1 (ppm)

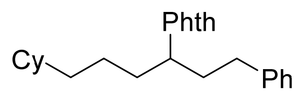
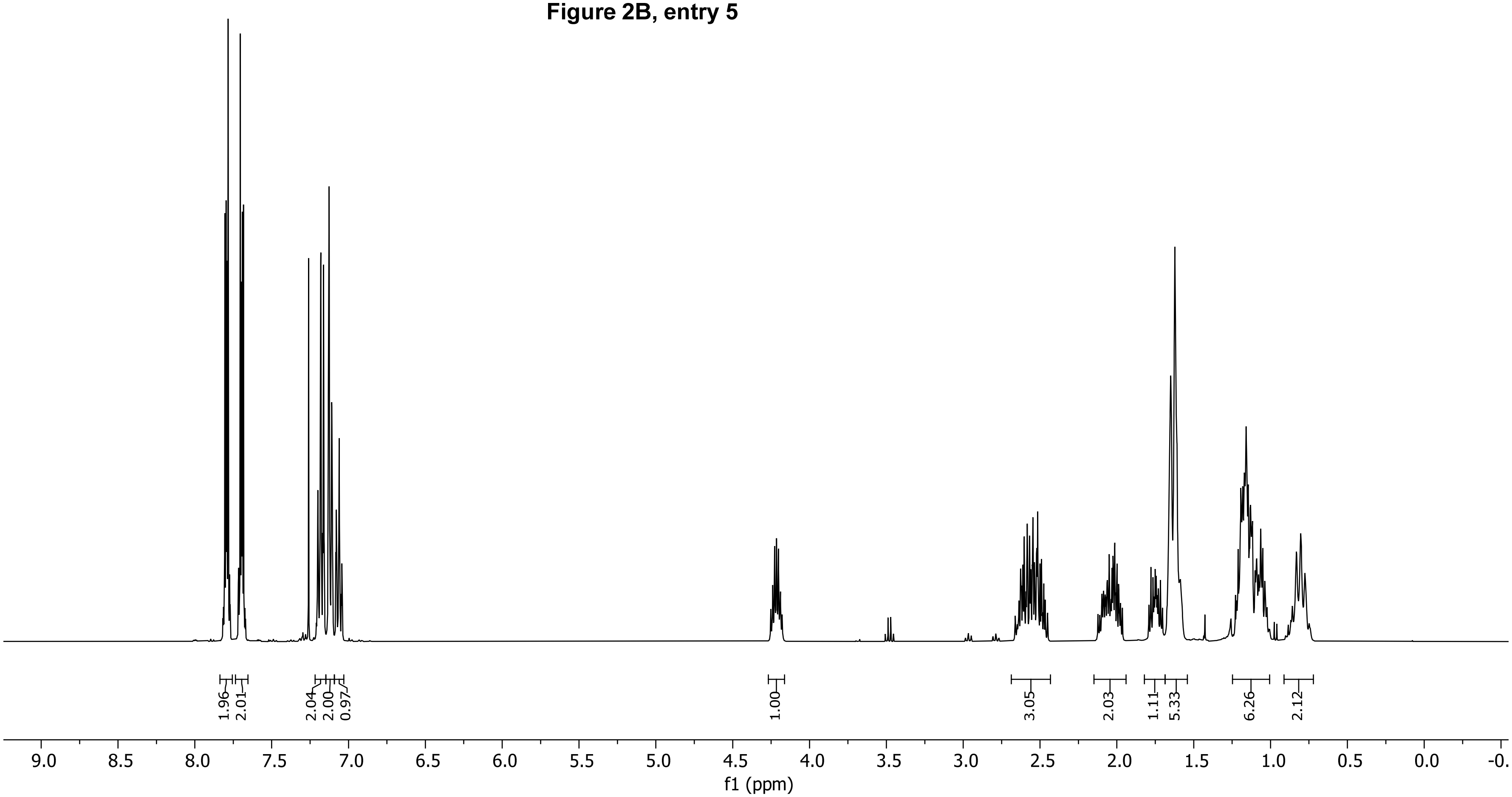


Figure 2B, entry 5



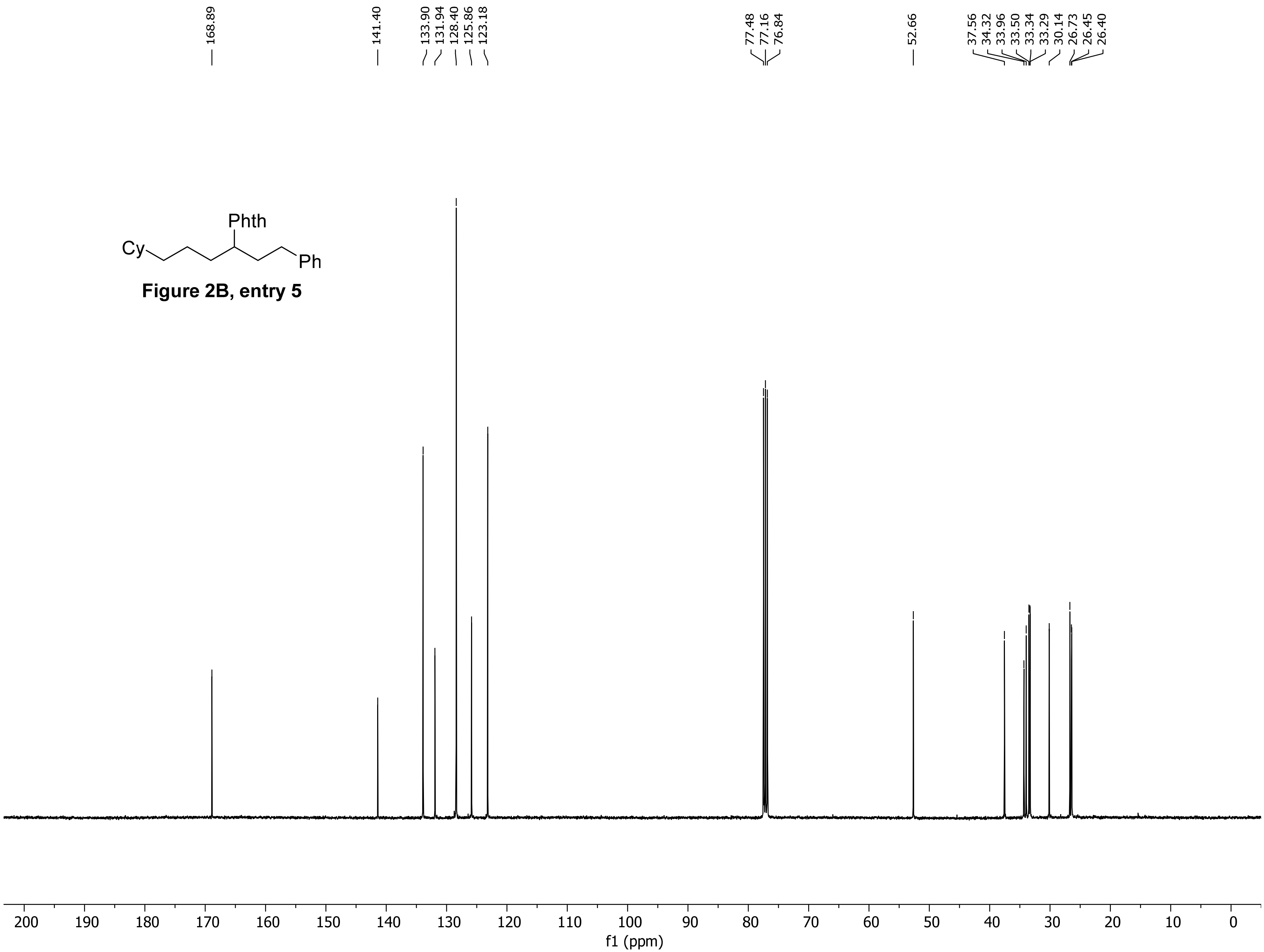


Figure 2B, entry 5

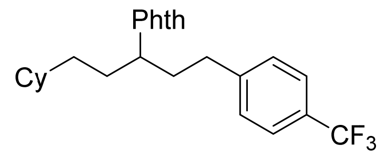
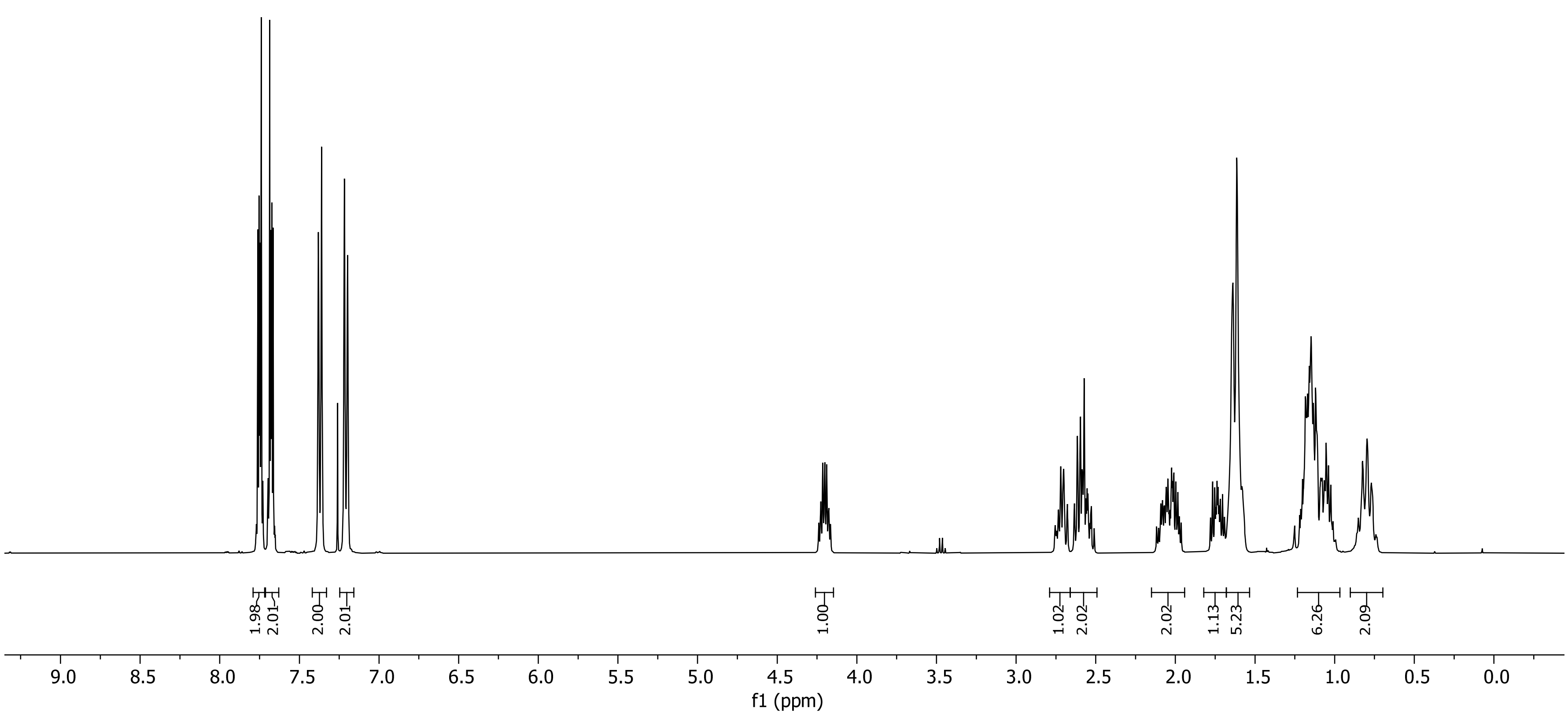


Figure 2B, entry 6



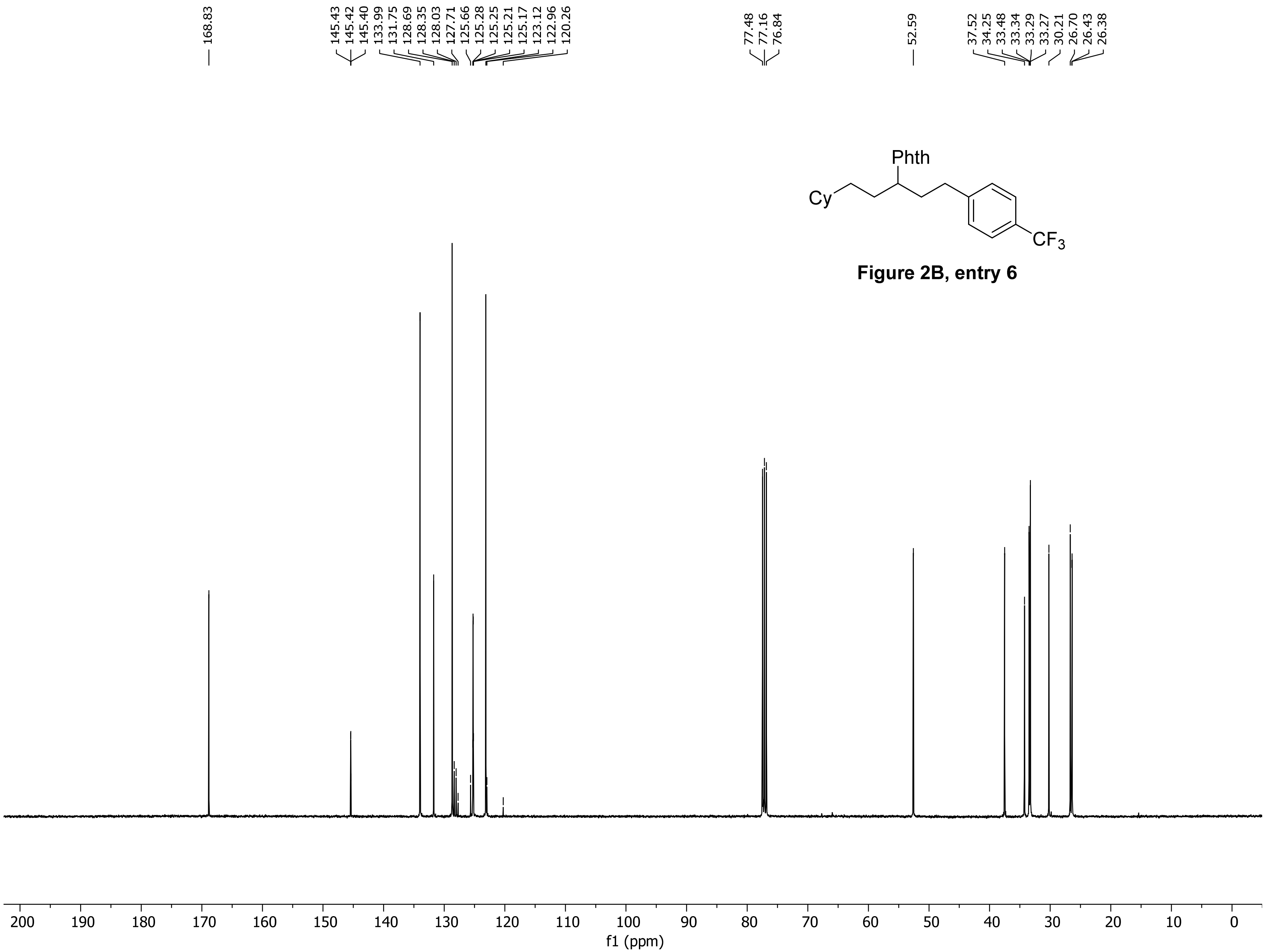


Figure 2B, entry 6

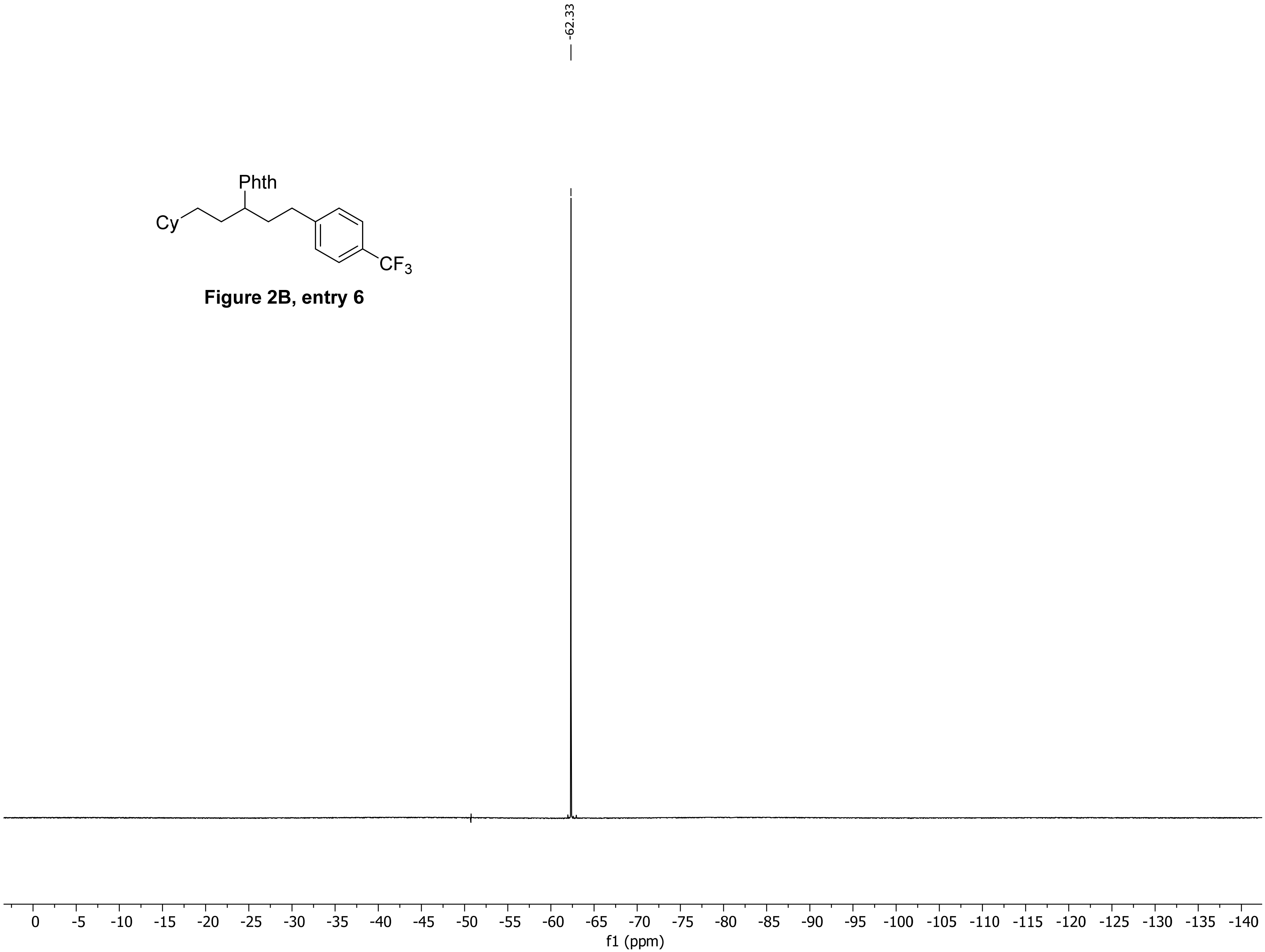


Figure 2B, entry 6

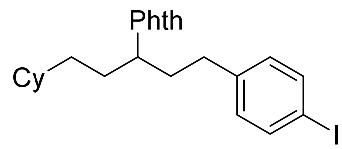
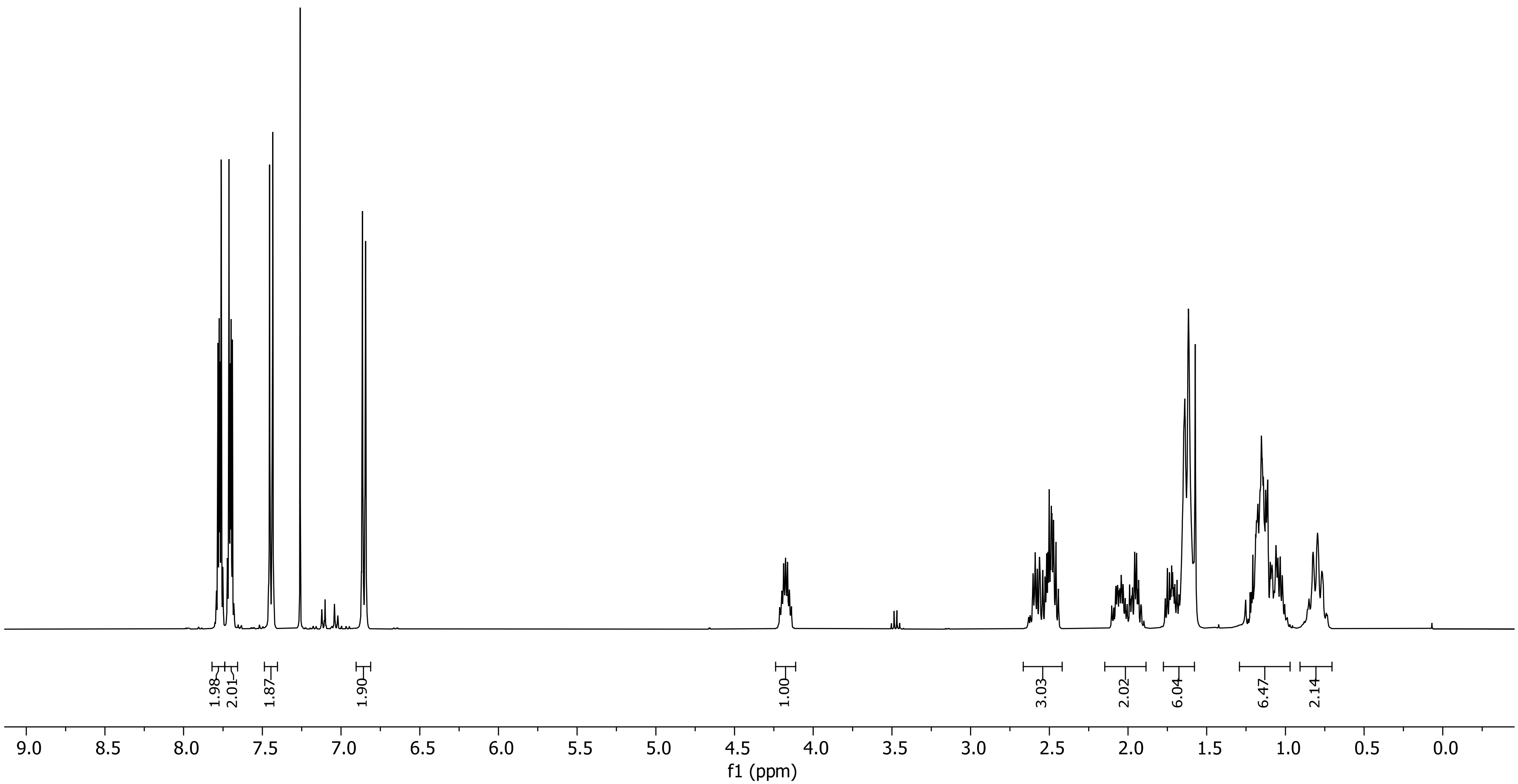


Figure 2B, entry 7



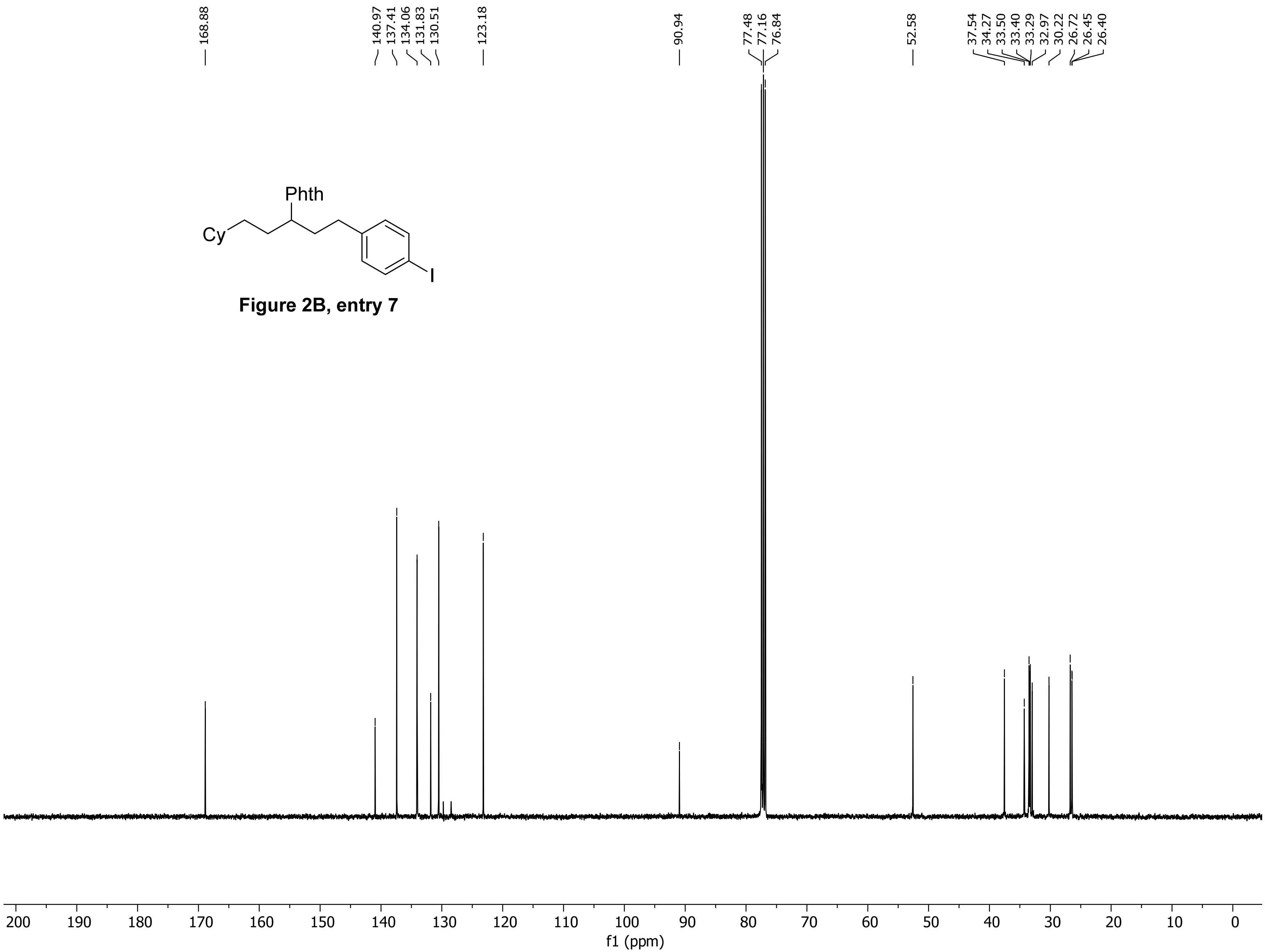


Figure 2B, entry 7

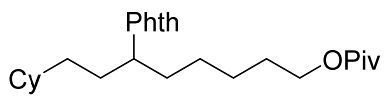
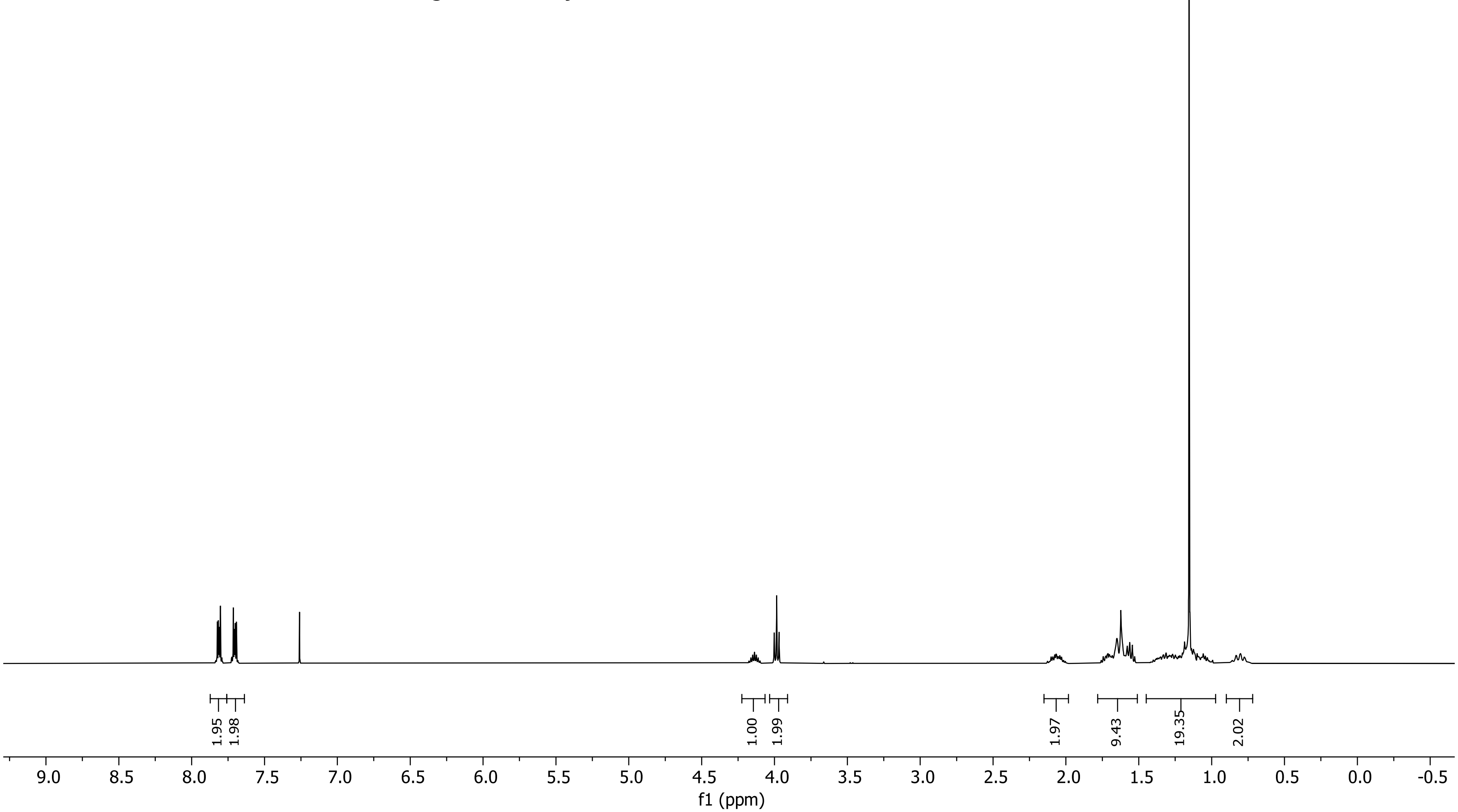
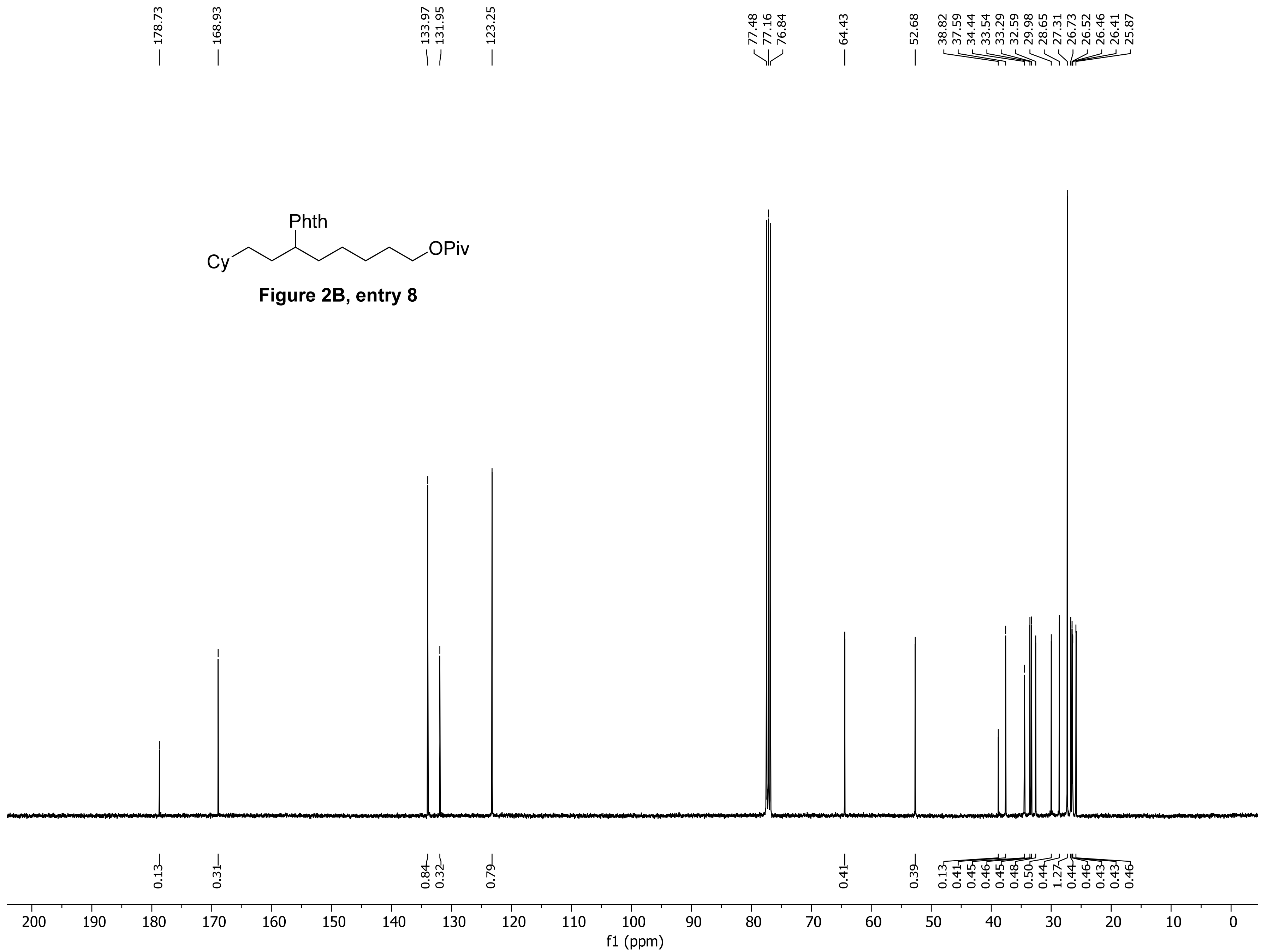


Figure 2B, entry 8




178.73
168.93
133.97
131.95
123.25
77.48
77.16
76.84
64.43
52.68
38.82
37.59
34.44
33.54
33.29
32.59
29.98
28.65
27.31
26.73
26.52
26.46
26.41
25.87
Phth
Cy
OPiv
Figure 2B, entry 8
0.13
0.31
0.84
0.32
0.79
0.41
0.39
0.13
0.41
0.45
0.46
0.45
0.48
0.50
0.44
1.27
0.44
0.46
0.43
0.43
0.46
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

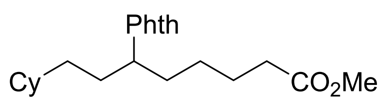
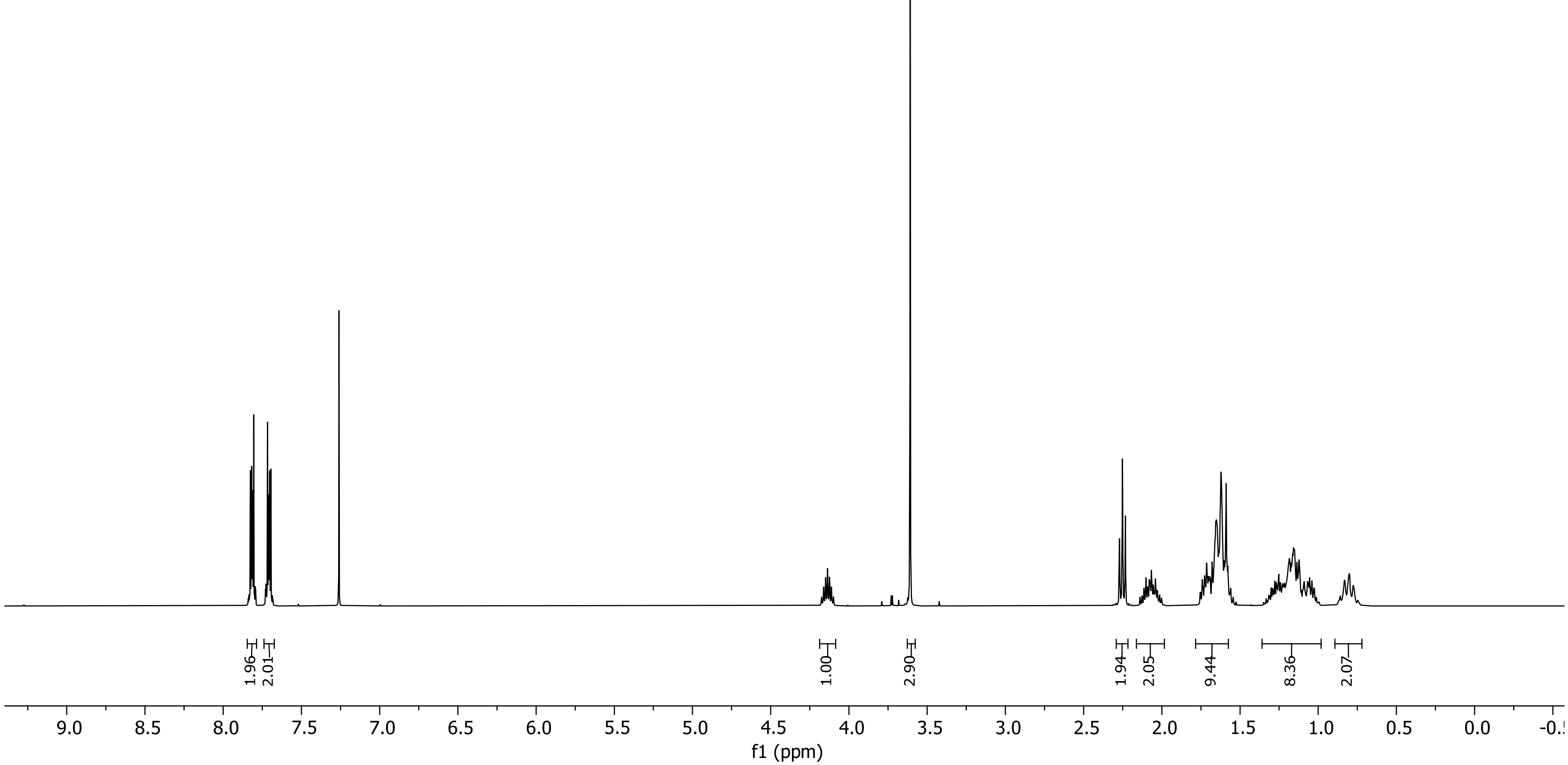
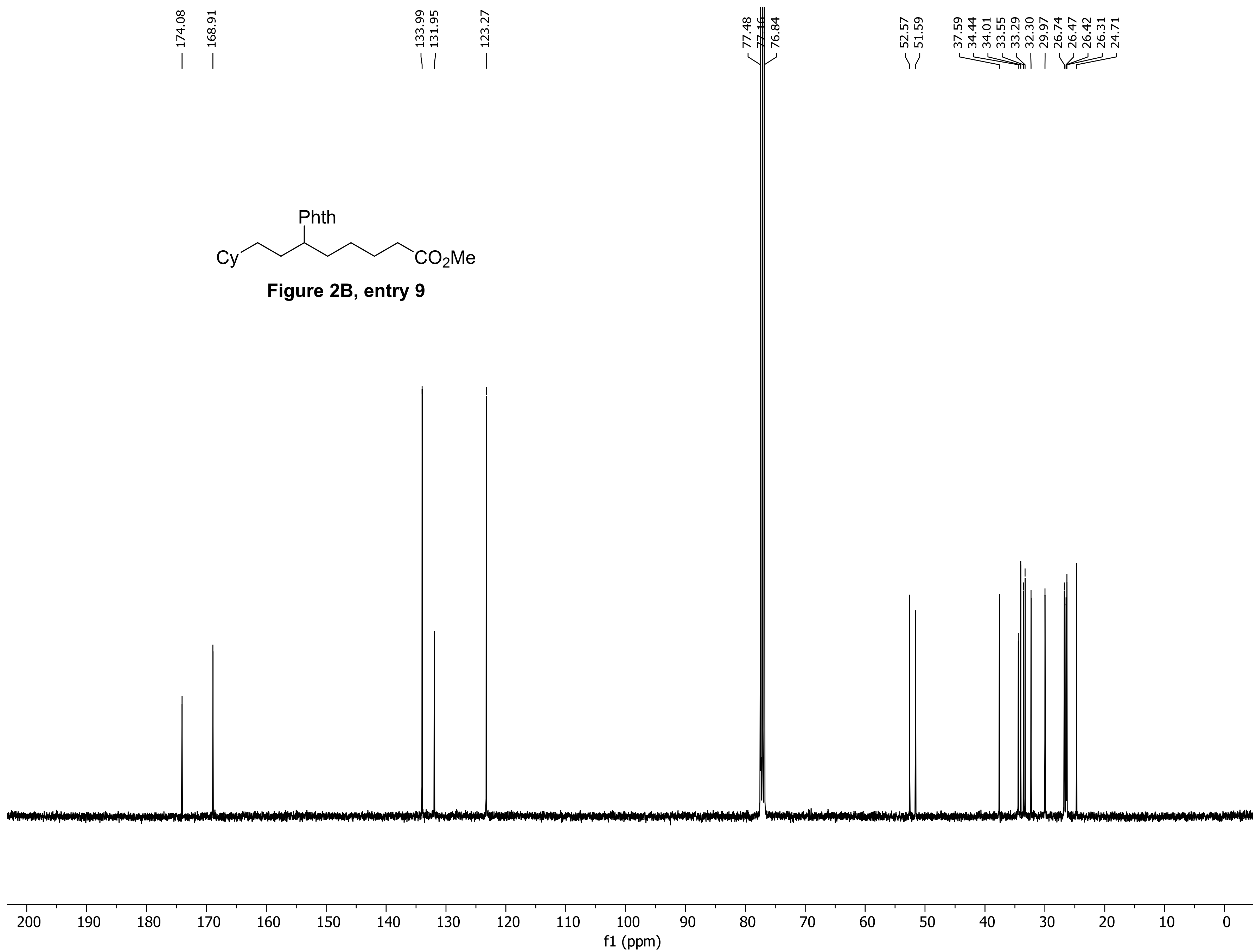
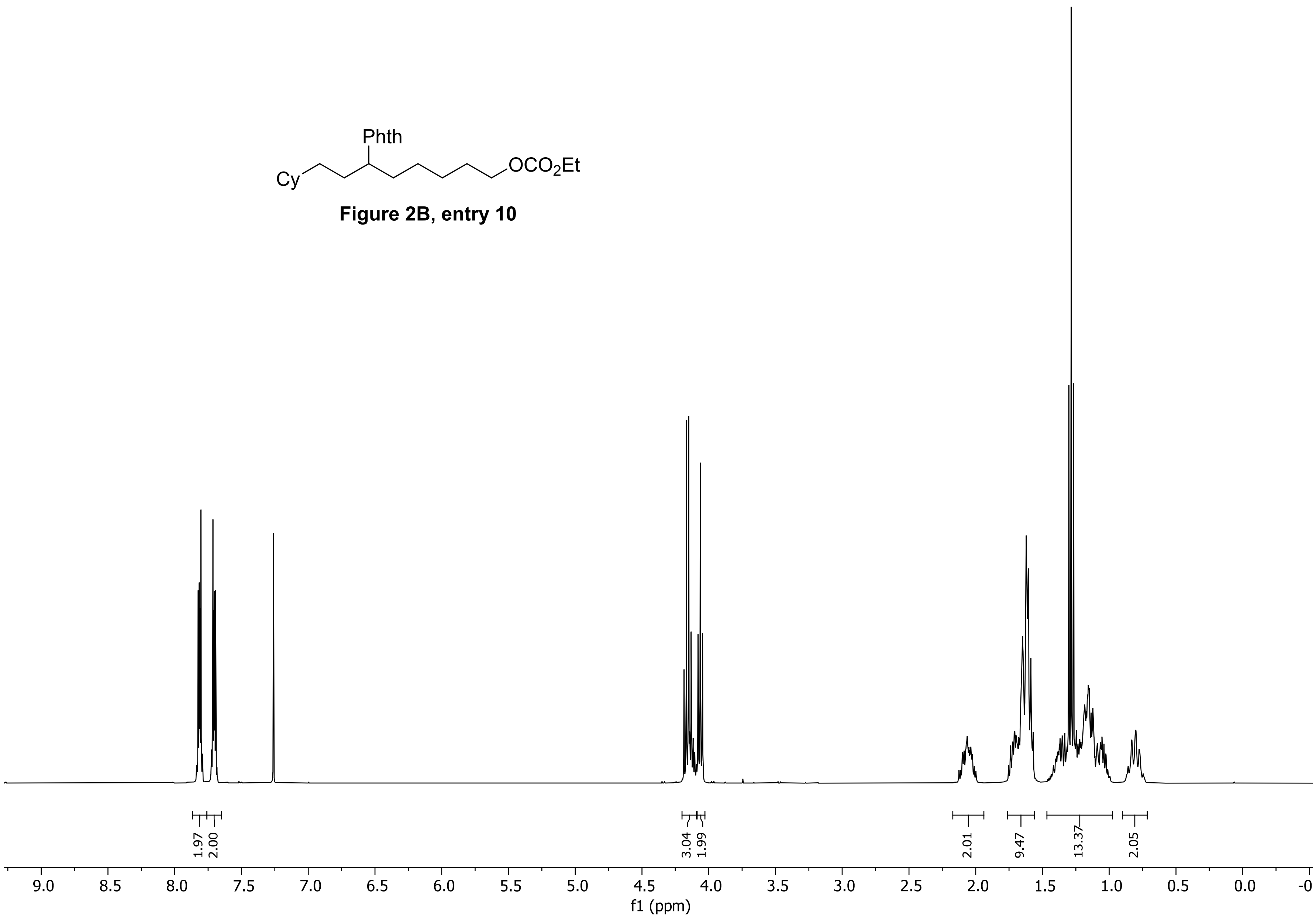


Figure 2B, entry 9




174.08
168.91
133.99
131.95
123.27
77.48
77.16
76.84
52.57
51.59
37.59
34.44
34.01
33.55
33.29
32.30
29.97
26.74
26.47
26.42
26.31
24.71
Phth
Cy
CO2Me
Figure 2B, entry 9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



Phth
Cy
OCO2Et
Figure 2B, entry 10
1.97
2.00
3.04
1.99
2.01
9.47
13.37
2.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

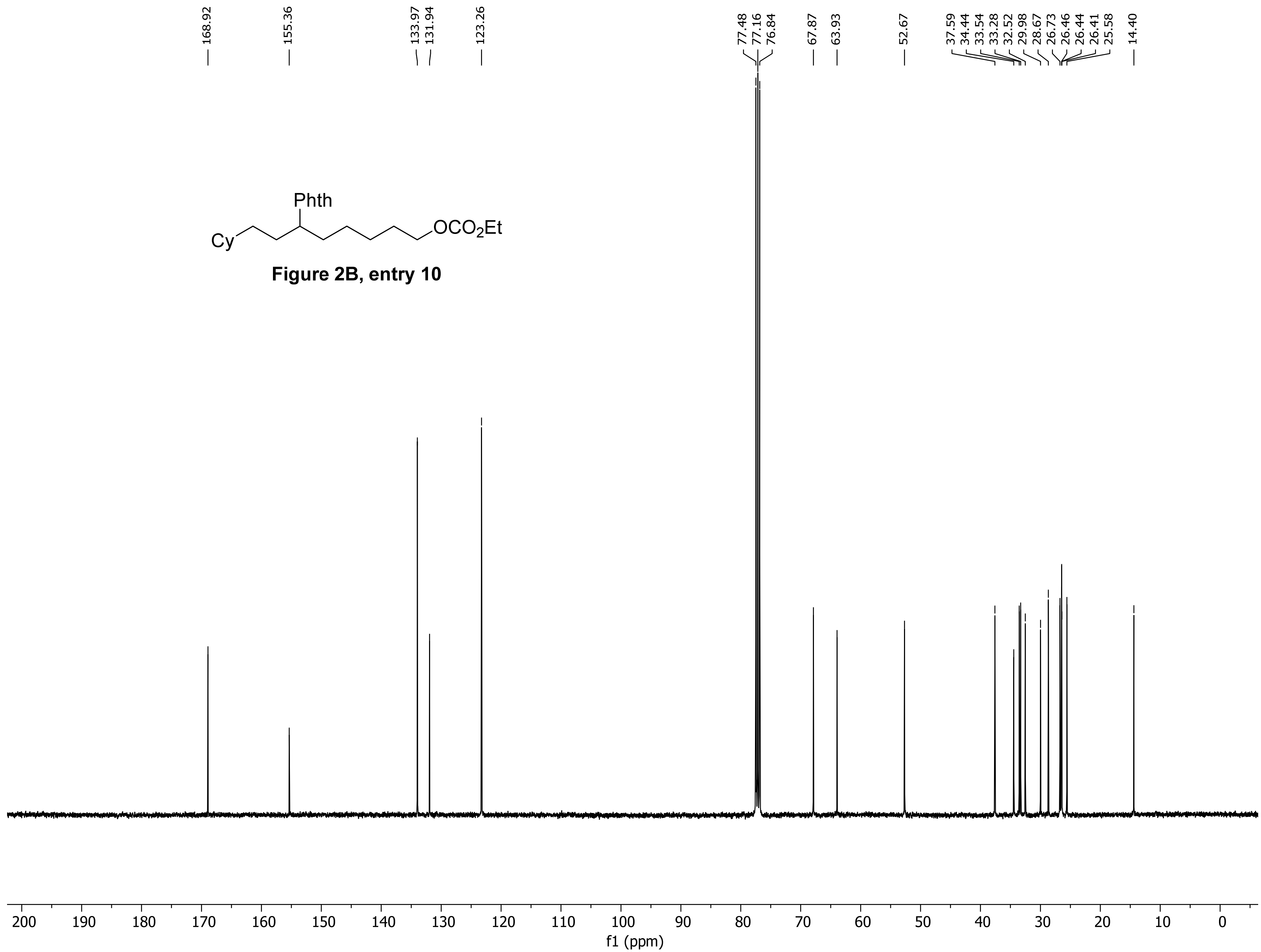
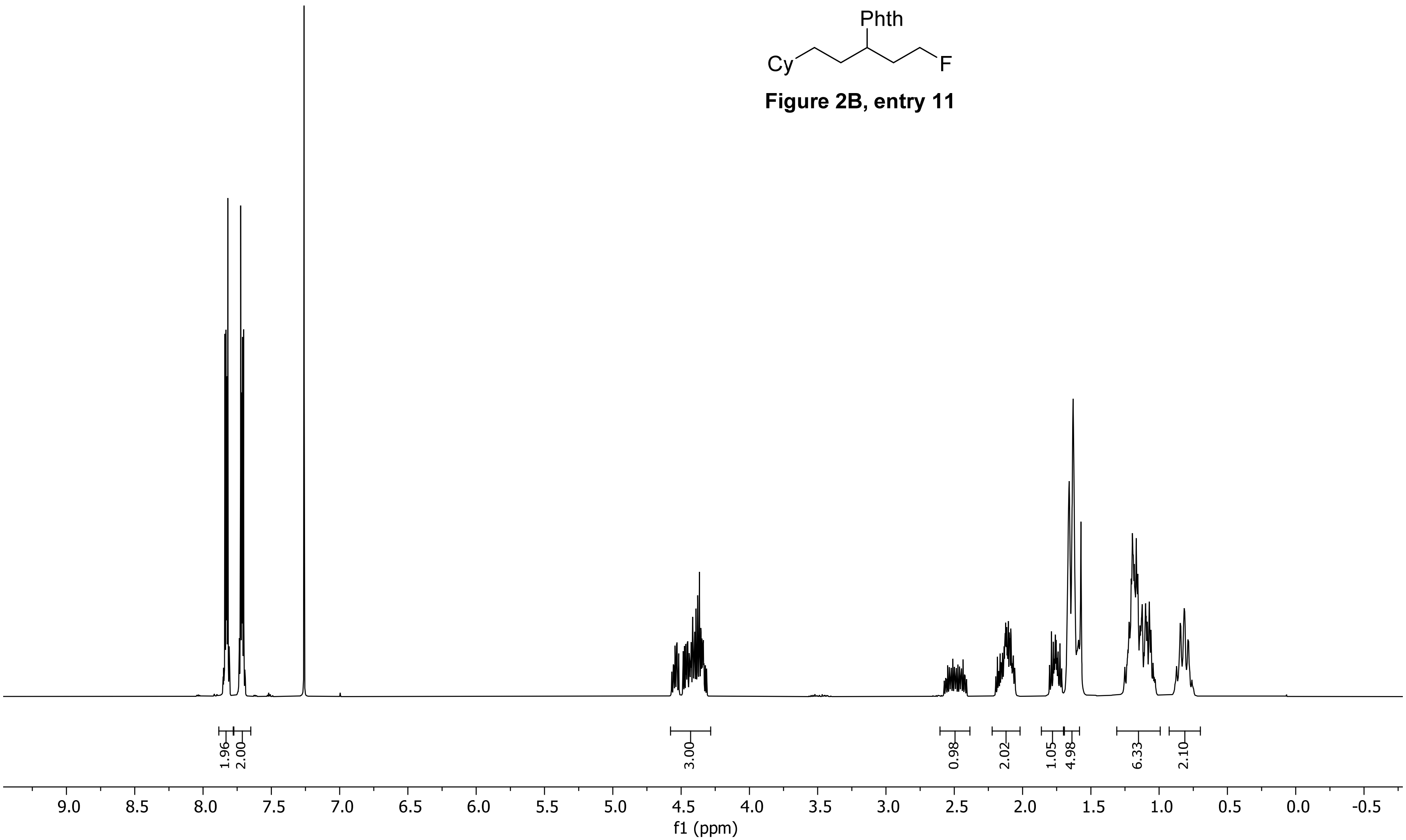
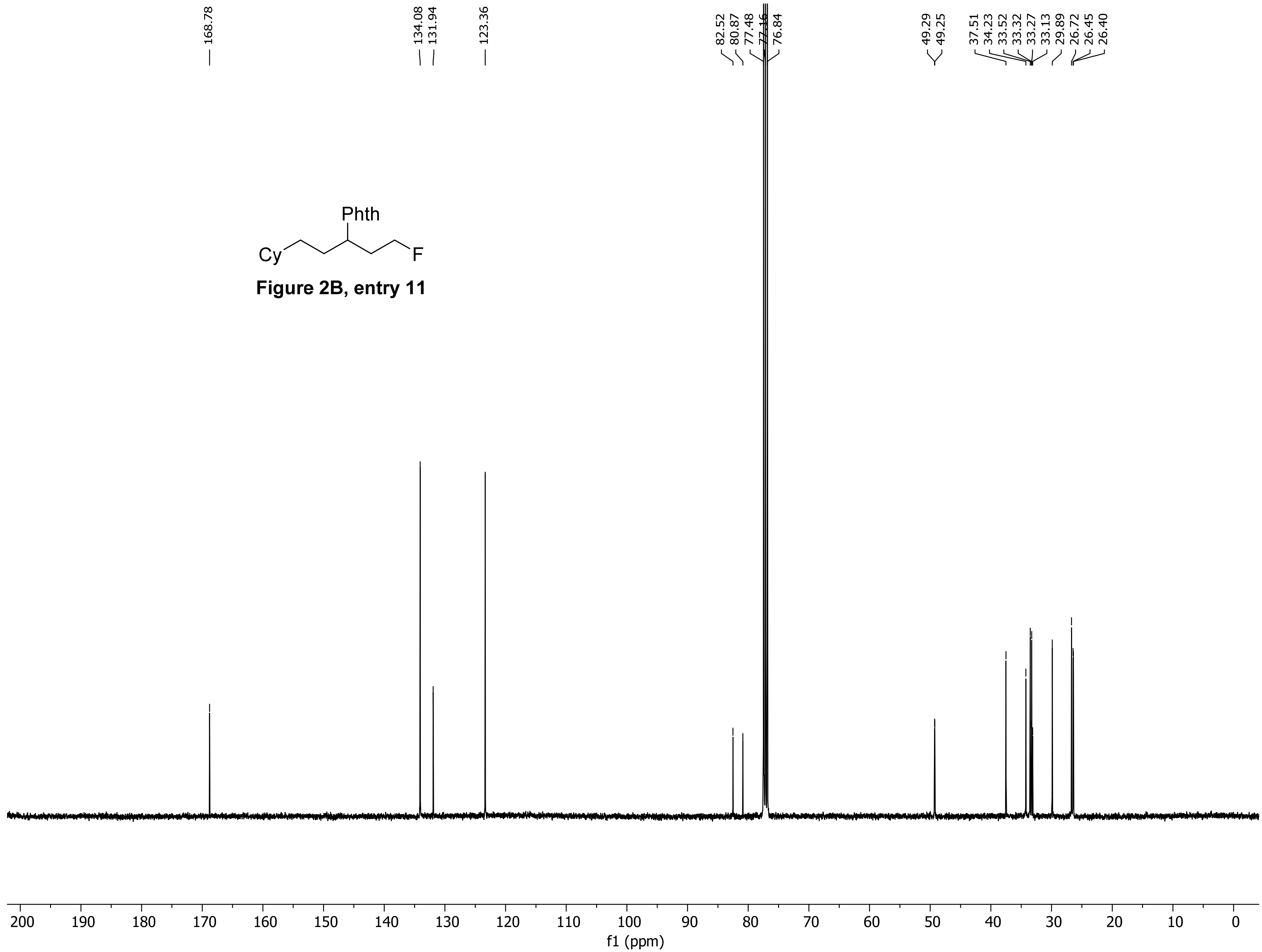


Figure 2B, entry 10


Phth
Cy
F
Figure 2B, entry 11
1.96
2.00
3.00
0.98
2.02
1.05
4.98
6.33
2.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


168.78
134.08
131.94
123.36
82.52
80.87
77.48
77.16
76.84
49.29
49.25
37.51
34.23
33.52
33.32
33.27
33.13
29.89
26.72
26.45
26.40
Phth
Cy
F
Figure 2B, entry 11
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

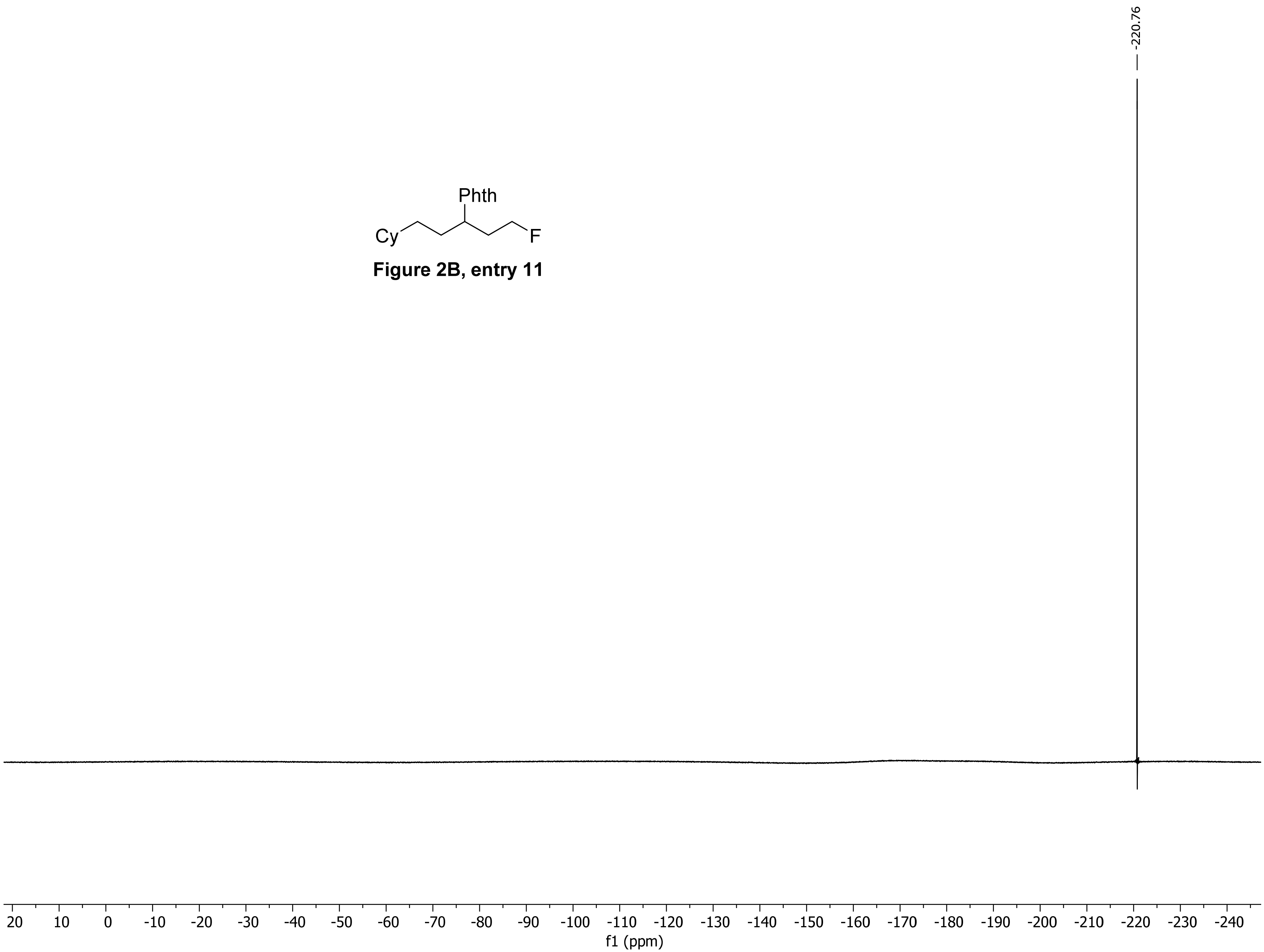


Figure 2B, entry 11

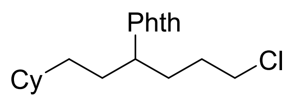
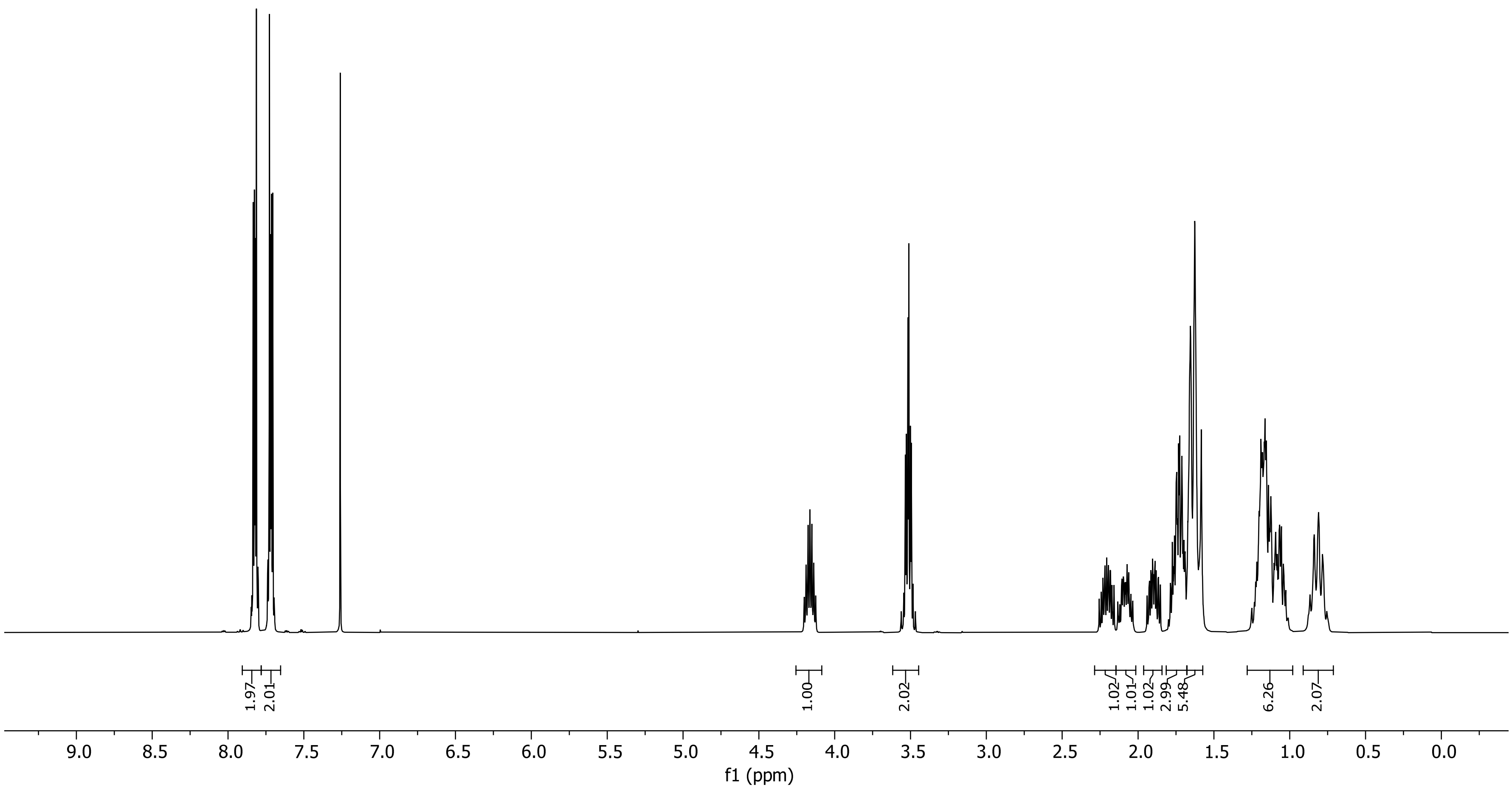


Figure 2B, entry 12



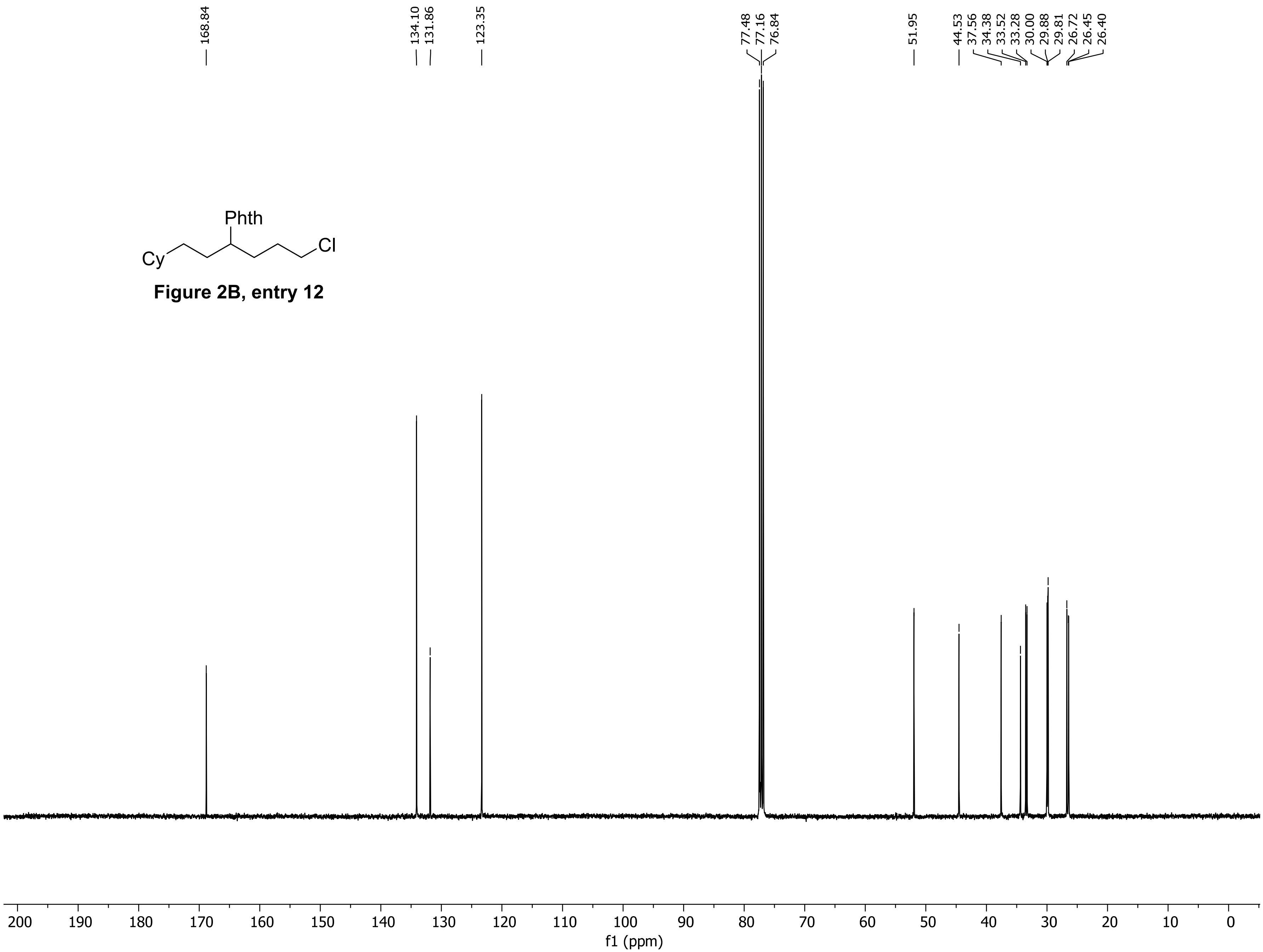
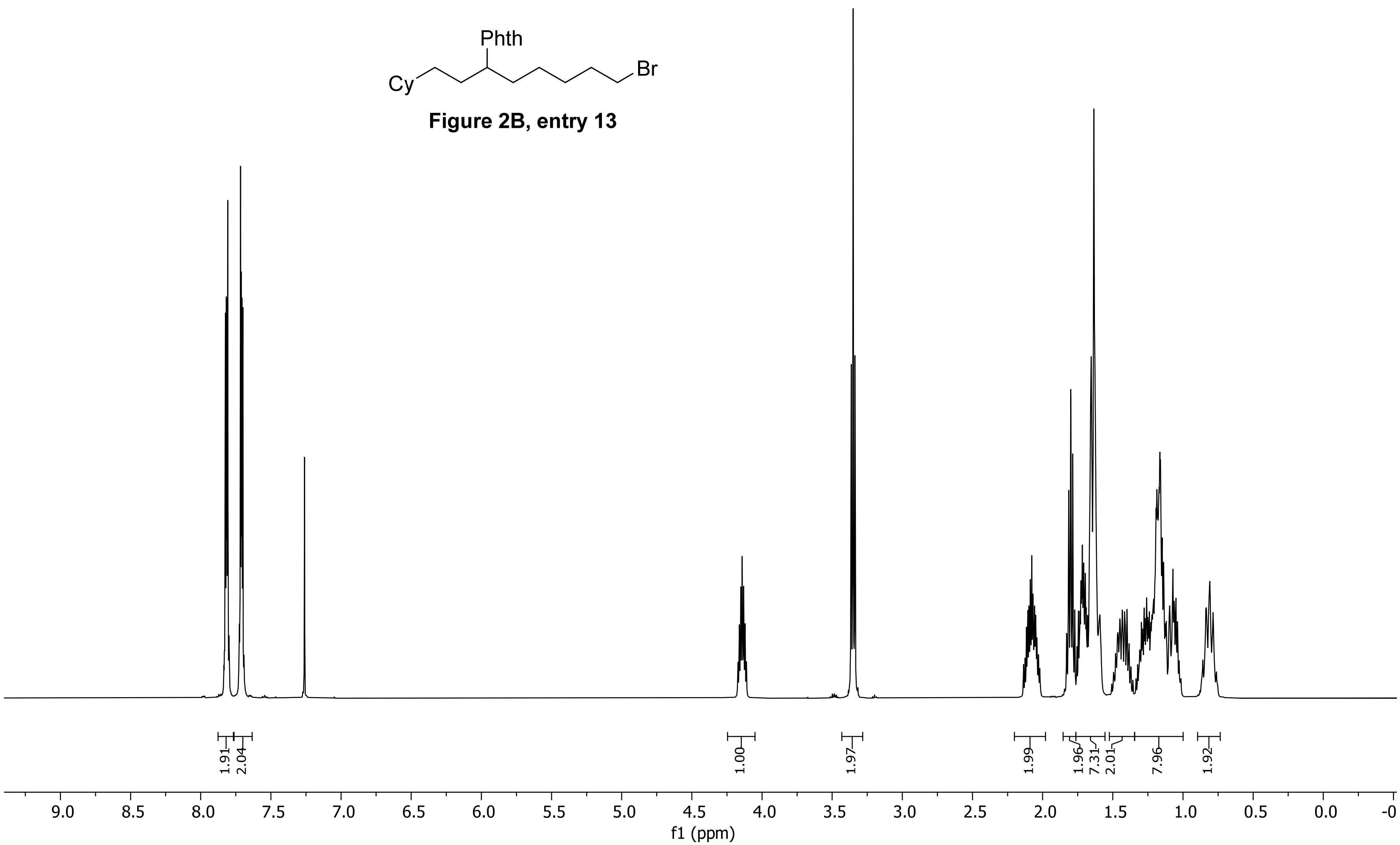
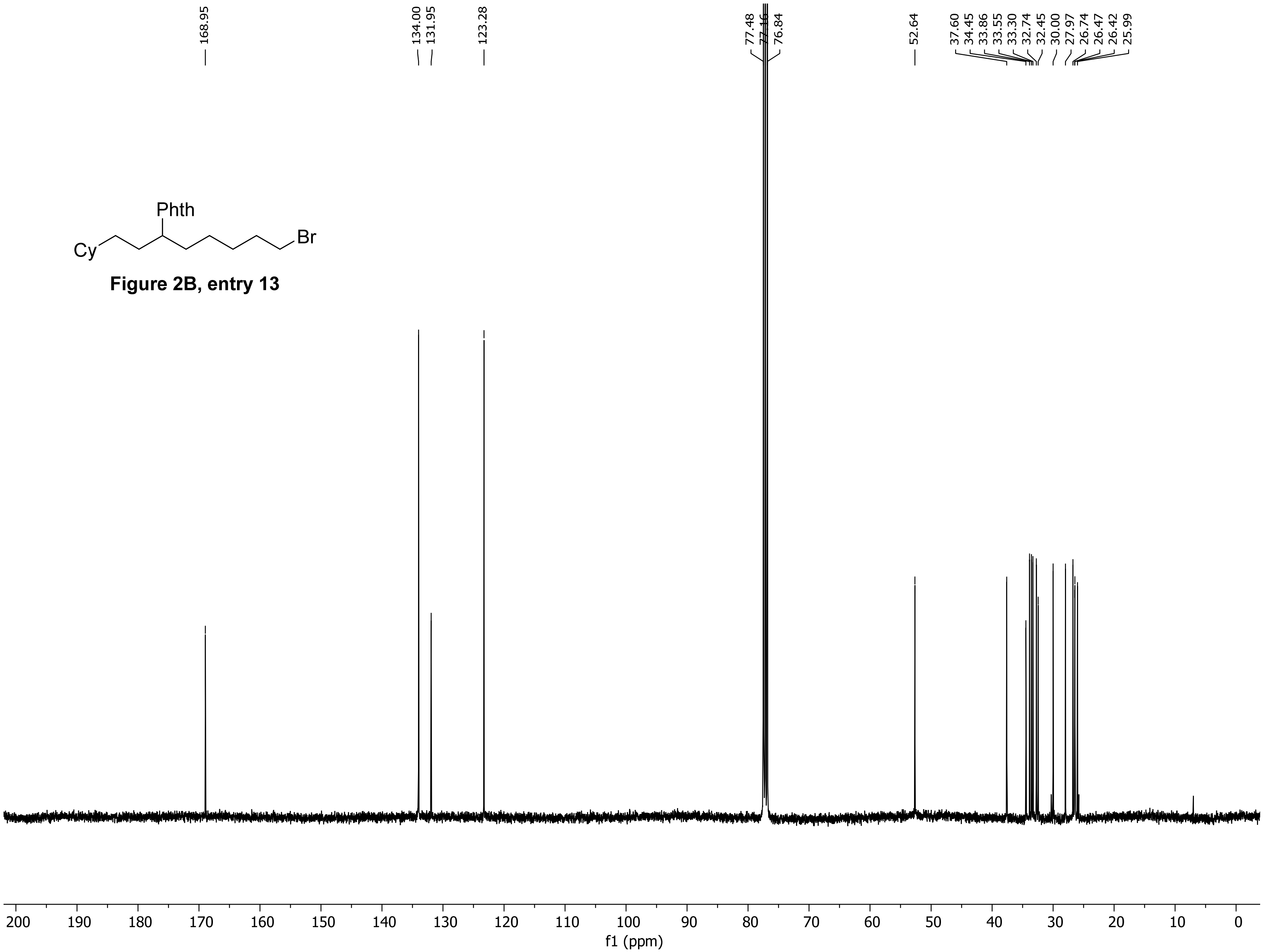


Figure 2B, entry 12


Phth
Cy
Br
Figure 2B, entry 13
1.91
2.04
1.00
1.97
1.99
1.96
7.31
2.01
7.96
1.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


Phth
Cy
Br
Figure 2B, entry 13
168.95
134.00
131.95
123.28
77.48
77.16
76.84
52.64
37.60
34.45
33.86
33.55
33.30
32.74
32.45
30.00
27.97
26.74
26.47
26.42
25.99
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

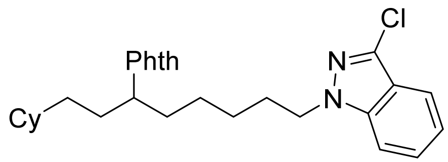
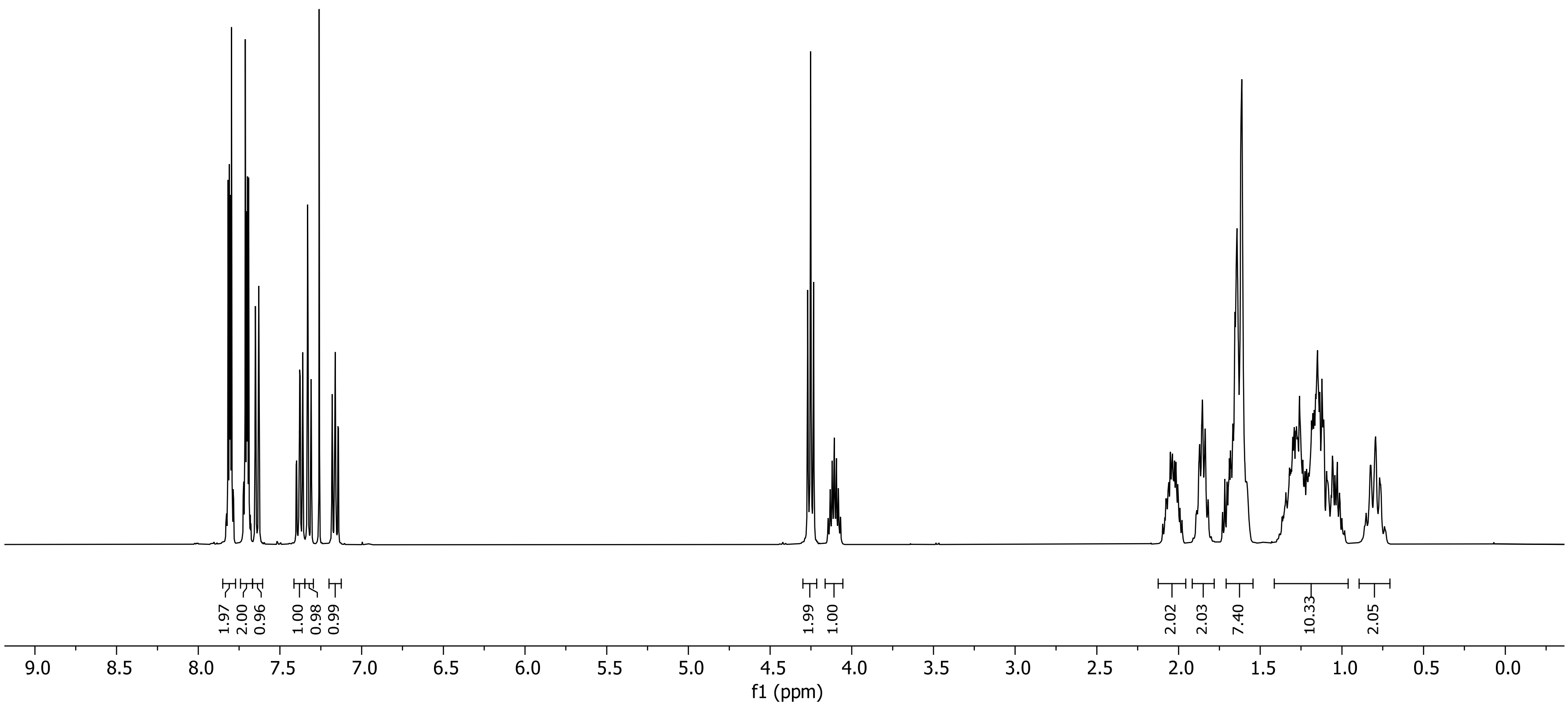


Figure 2B, entry 14



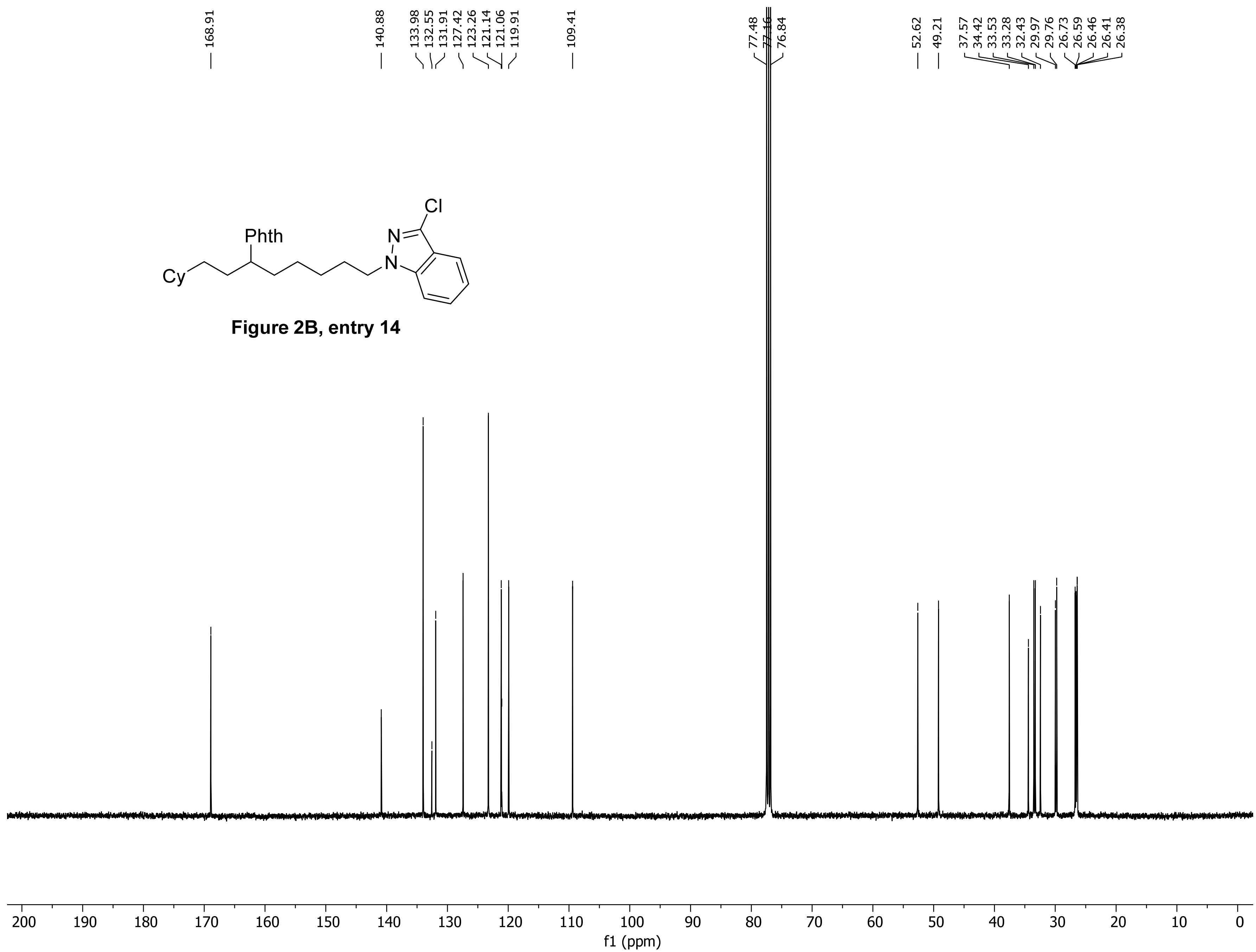


Figure 2B, entry 14

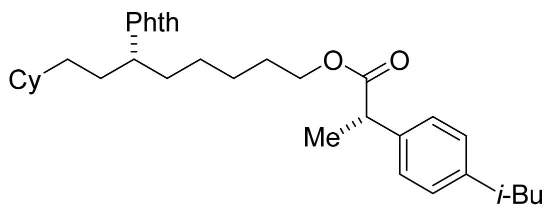
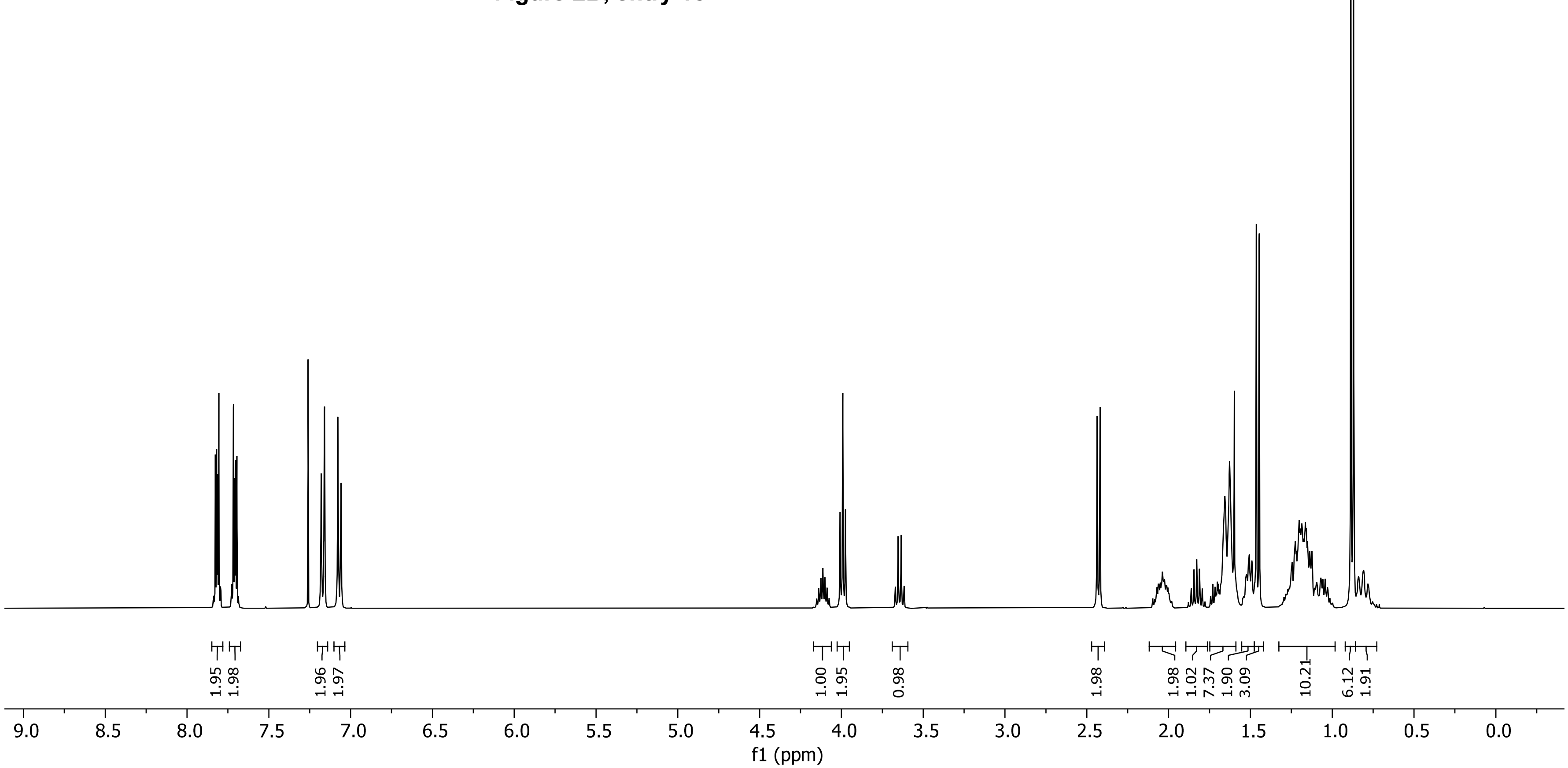
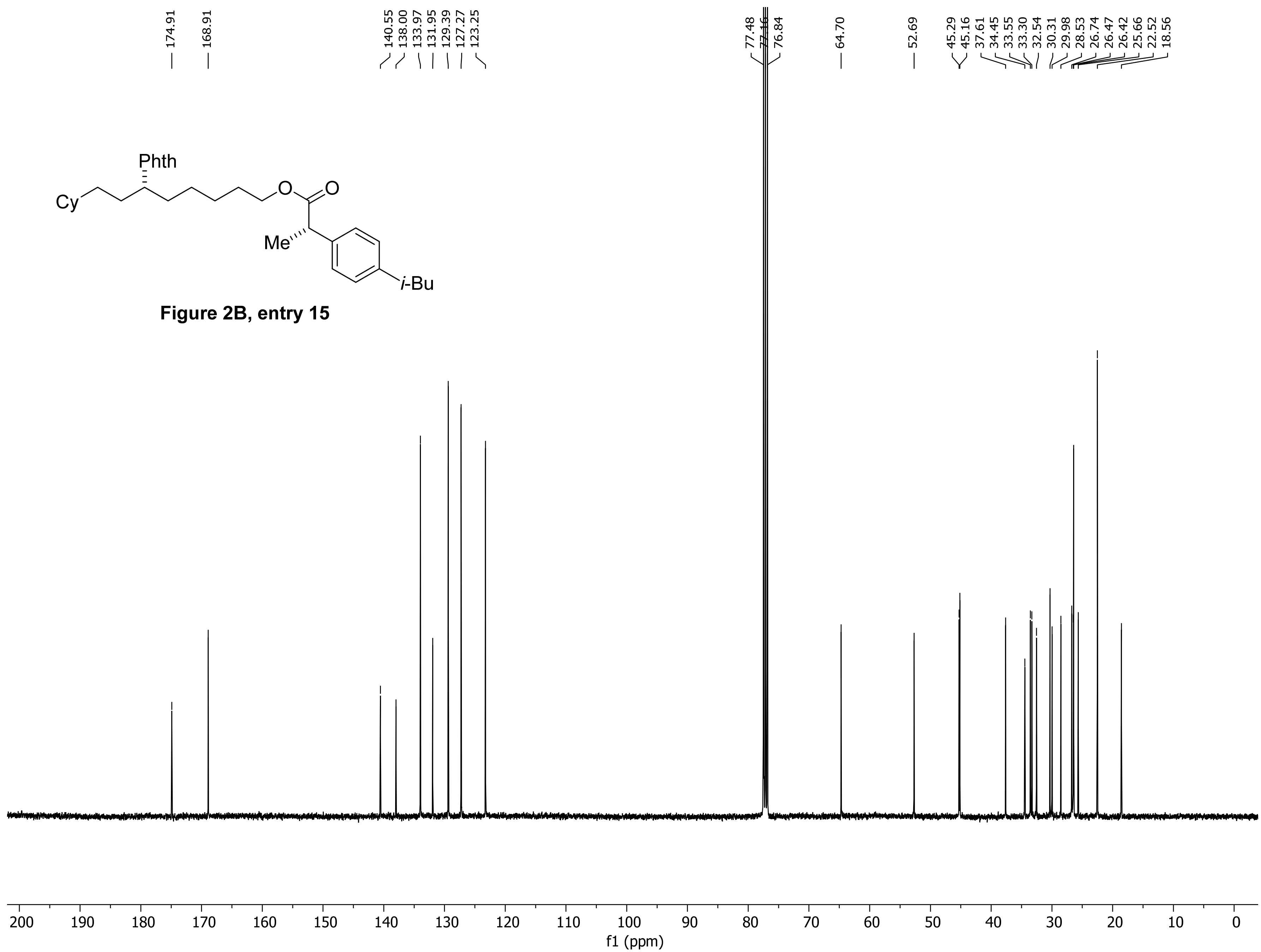


Figure 2B, entry 15





174.91
168.91
140.55
138.00
133.97
131.95
129.39
127.27
123.25
77.48
77.16
76.84
64.70
52.69
45.29
45.16
37.61
34.45
33.55
33.30
32.54
30.31
29.98
28.53
26.74
26.47
26.42
25.66
22.52
18.56
Phth
Cy
O
O
Me
i-Bu
Figure 2B, entry 15
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

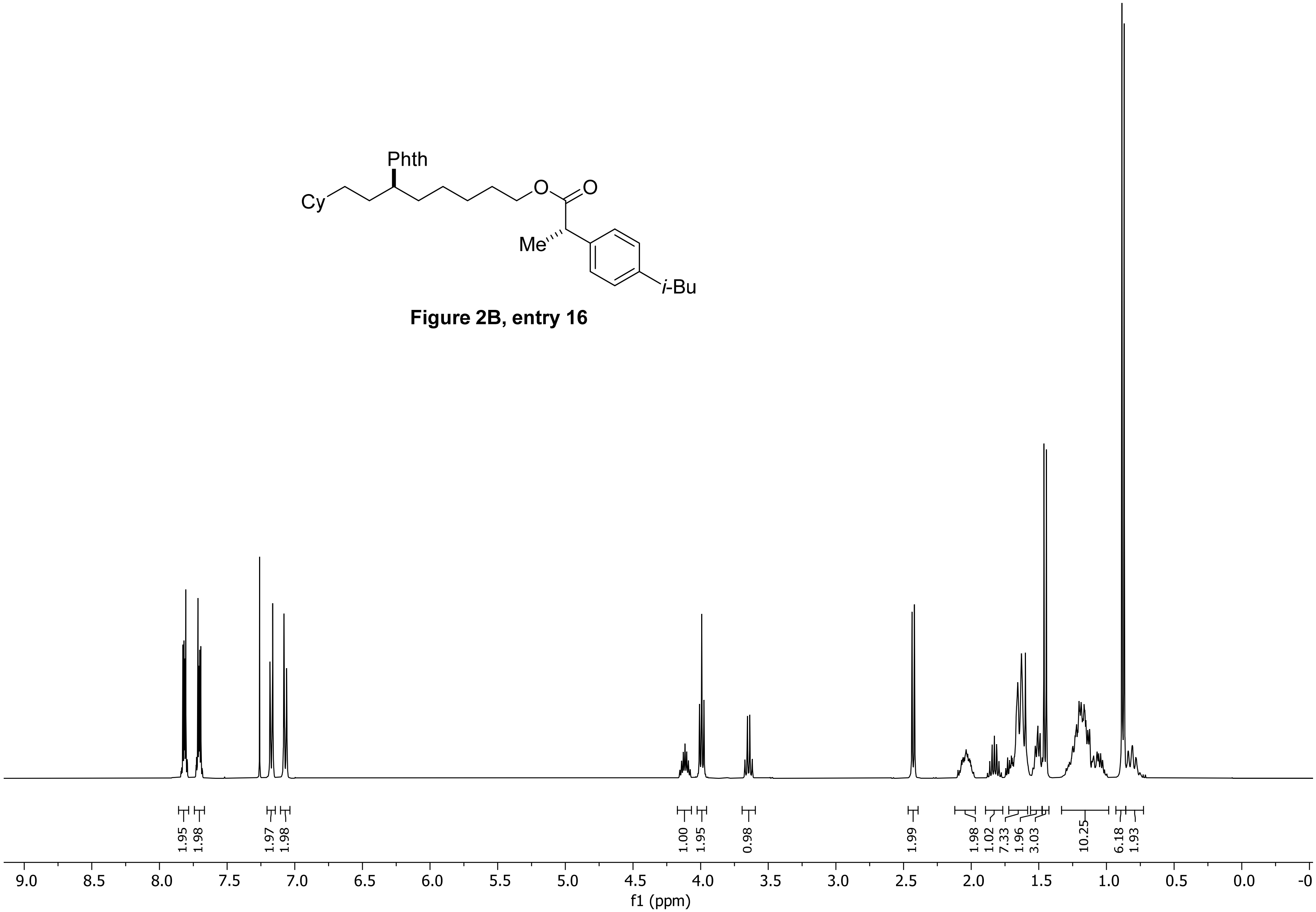
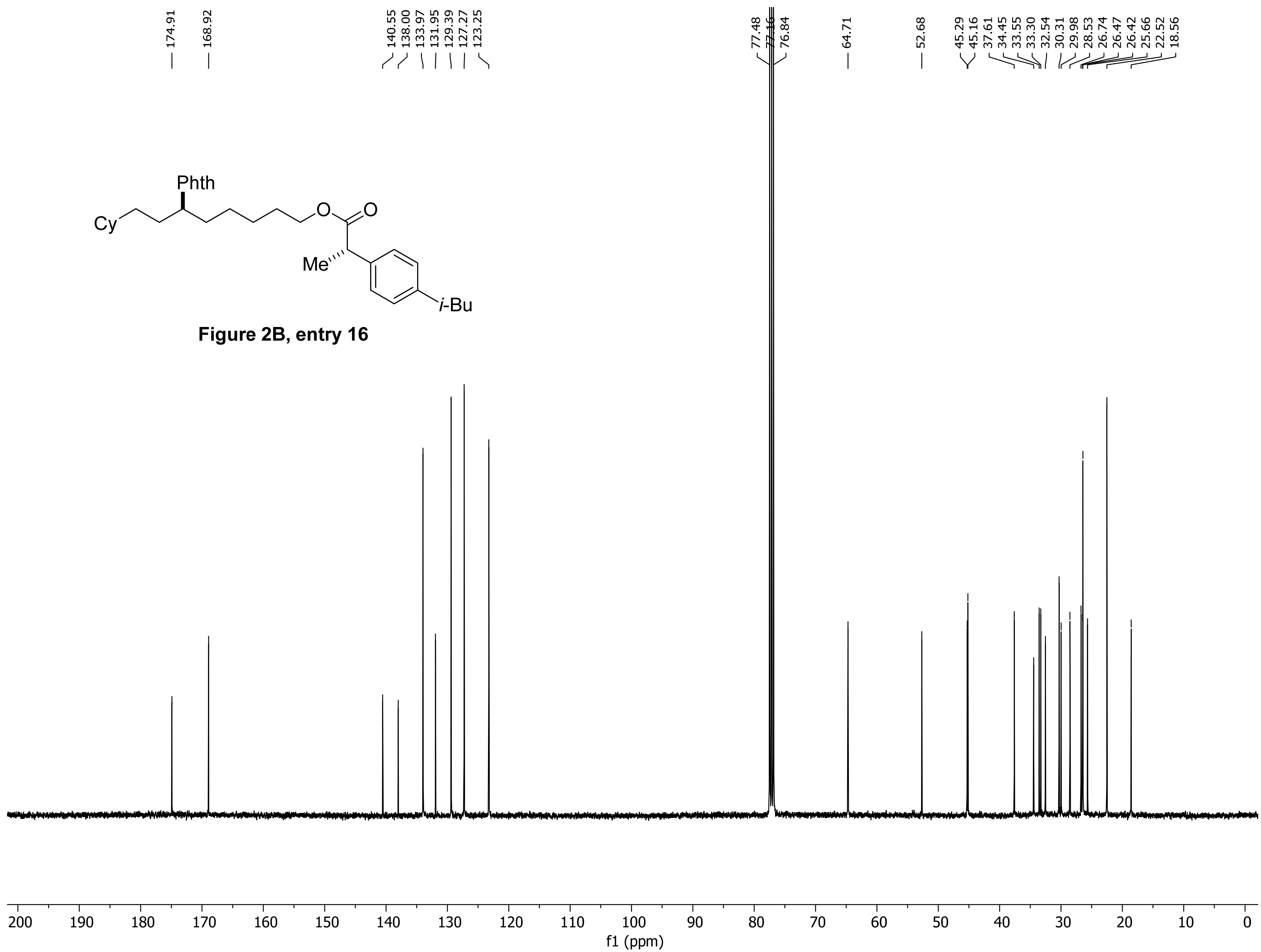


Figure 2B, entry 16


174.91
168.92
140.55
138.00
133.97
131.95
129.39
127.27
123.25
77.48
77.16
76.84
64.71
52.68
45.29
45.16
37.61
34.45
33.55
33.30
32.54
30.31
29.98
28.53
26.74
26.47
26.42
25.66
22.52
18.56
Phth
Cy
O
O
Me
i-Bu
Figure 2B, entry 16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

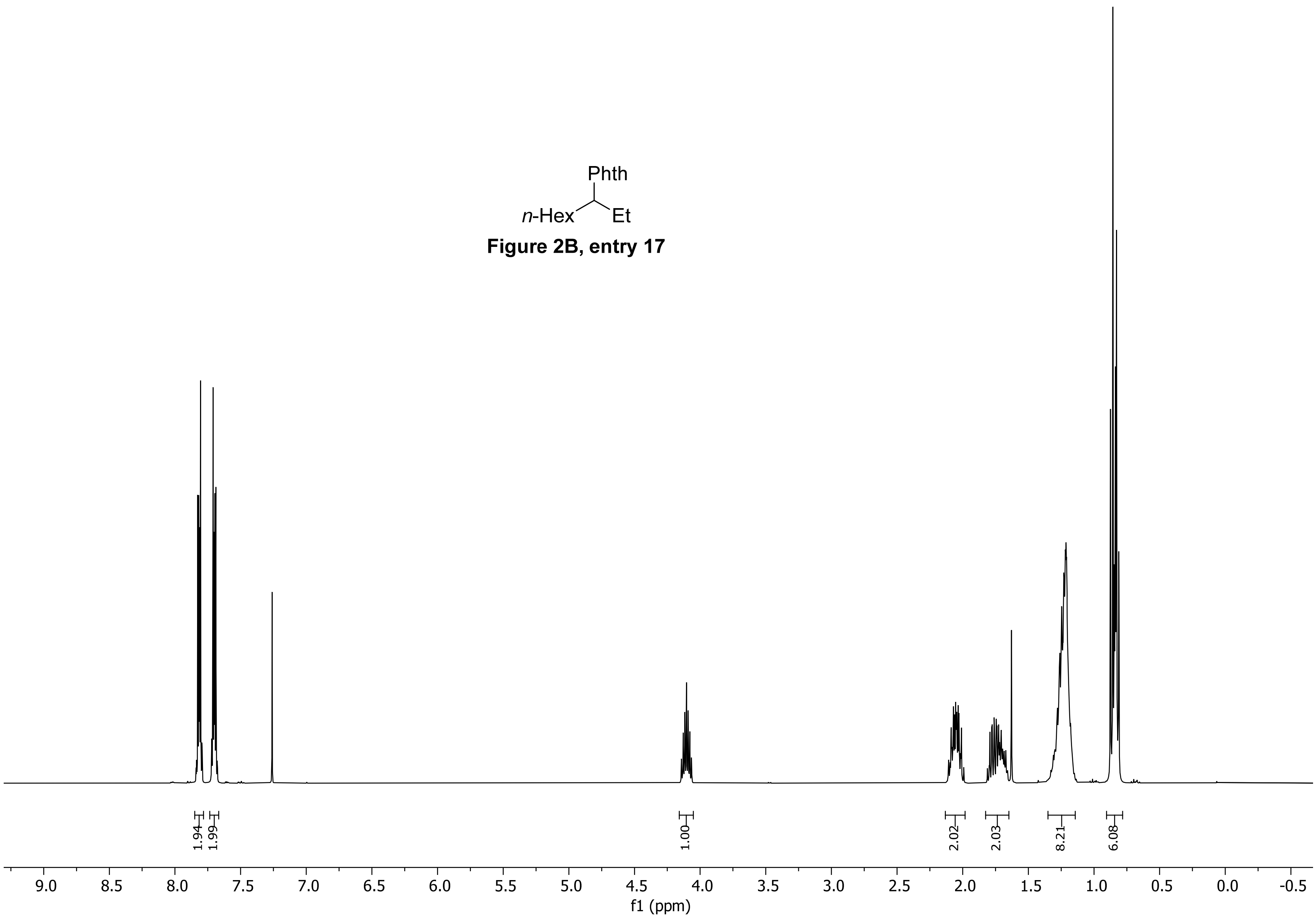


Figure 2B, entry 17

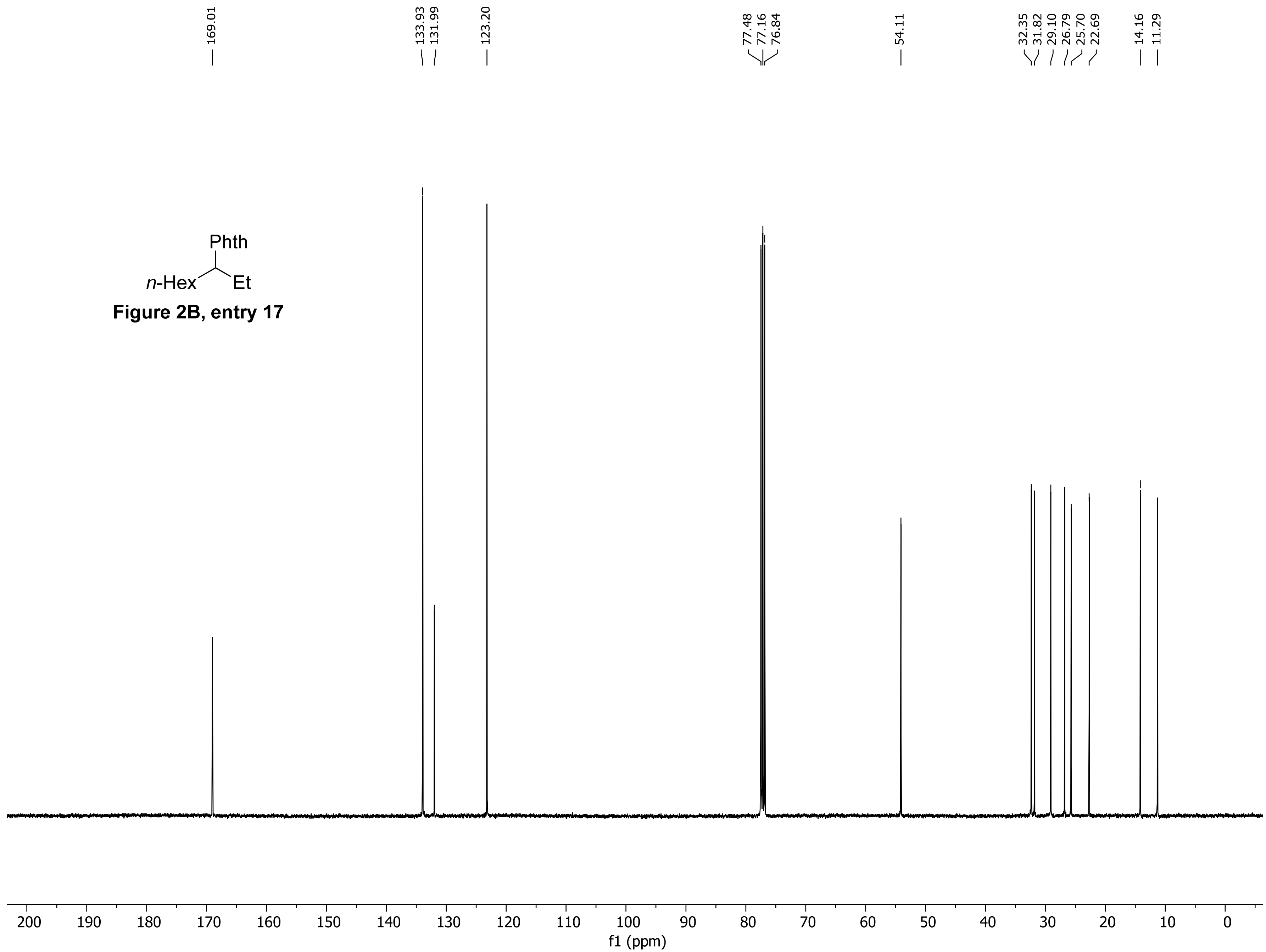
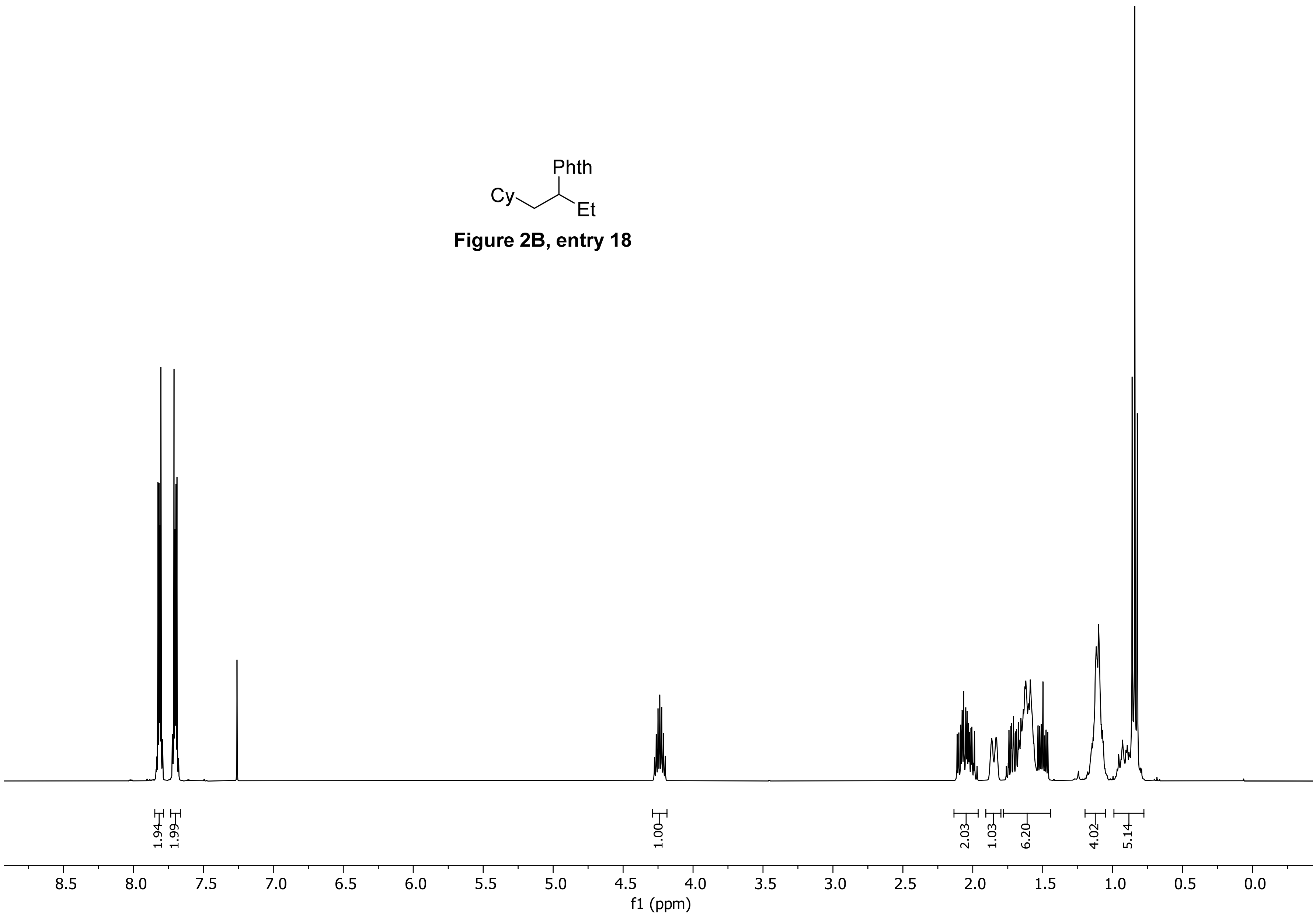
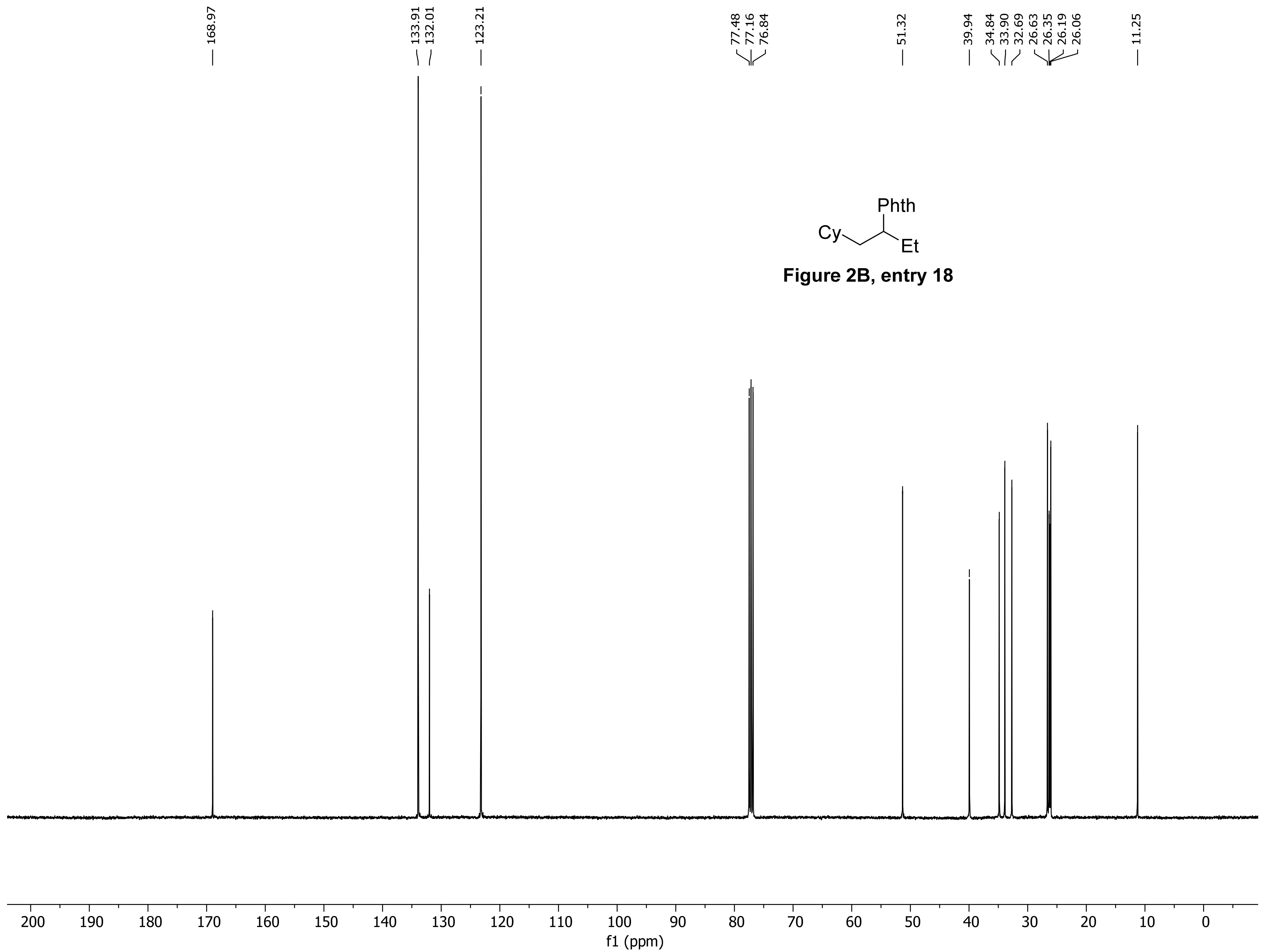


Figure 2B, entry 17



Phth
Cy
Et
Figure 2B, entry 18
1.94
1.99
1.00
2.03
1.03
6.20
4.02
5.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.97
133.91
132.01
123.21
77.48
77.16
76.84
51.32
39.94
34.84
33.90
32.69
26.63
26.35
26.19
26.06
11.25
Phth
Cy
Et
Figure 2B, entry 18
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

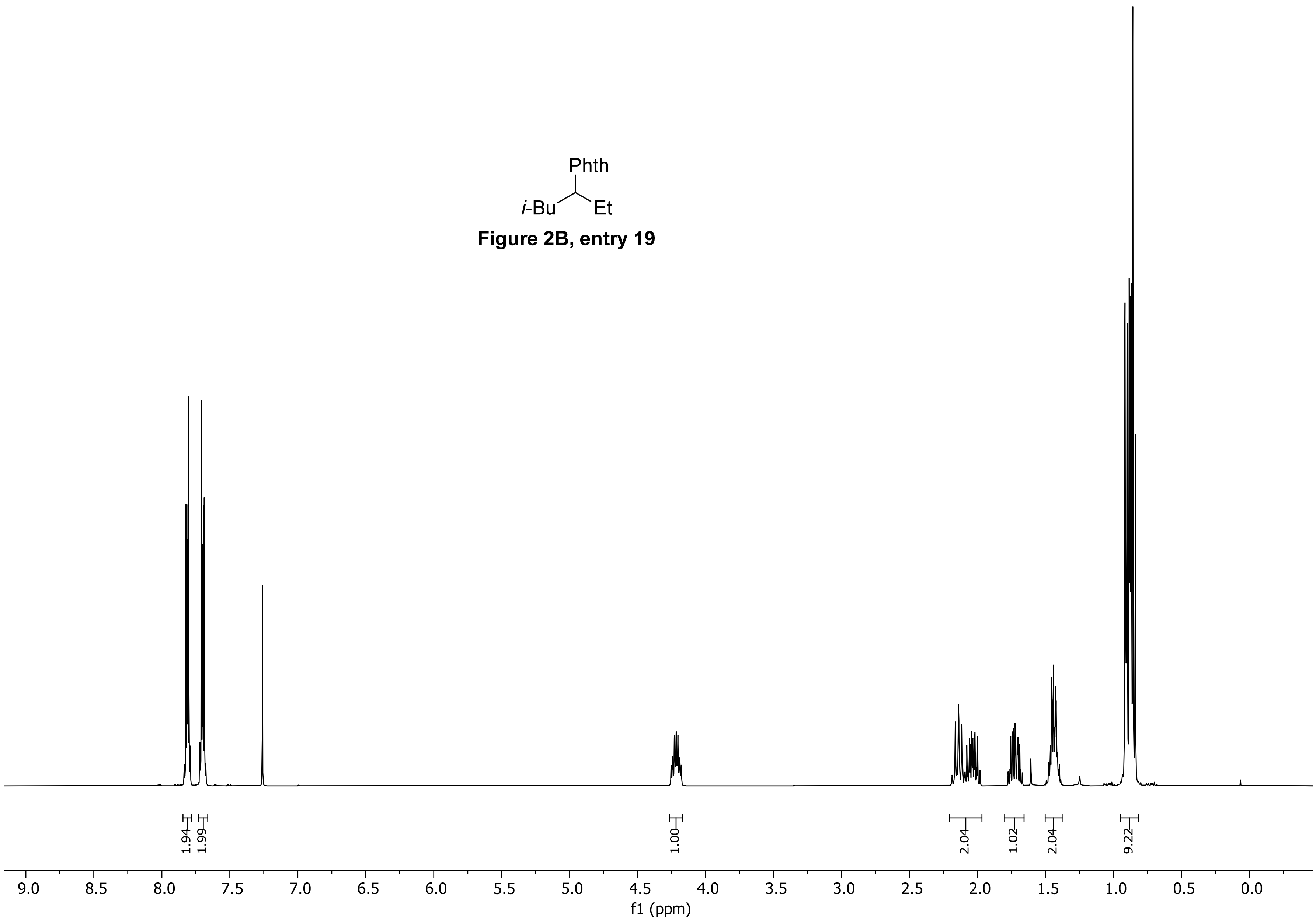


Figure 2B, entry 19

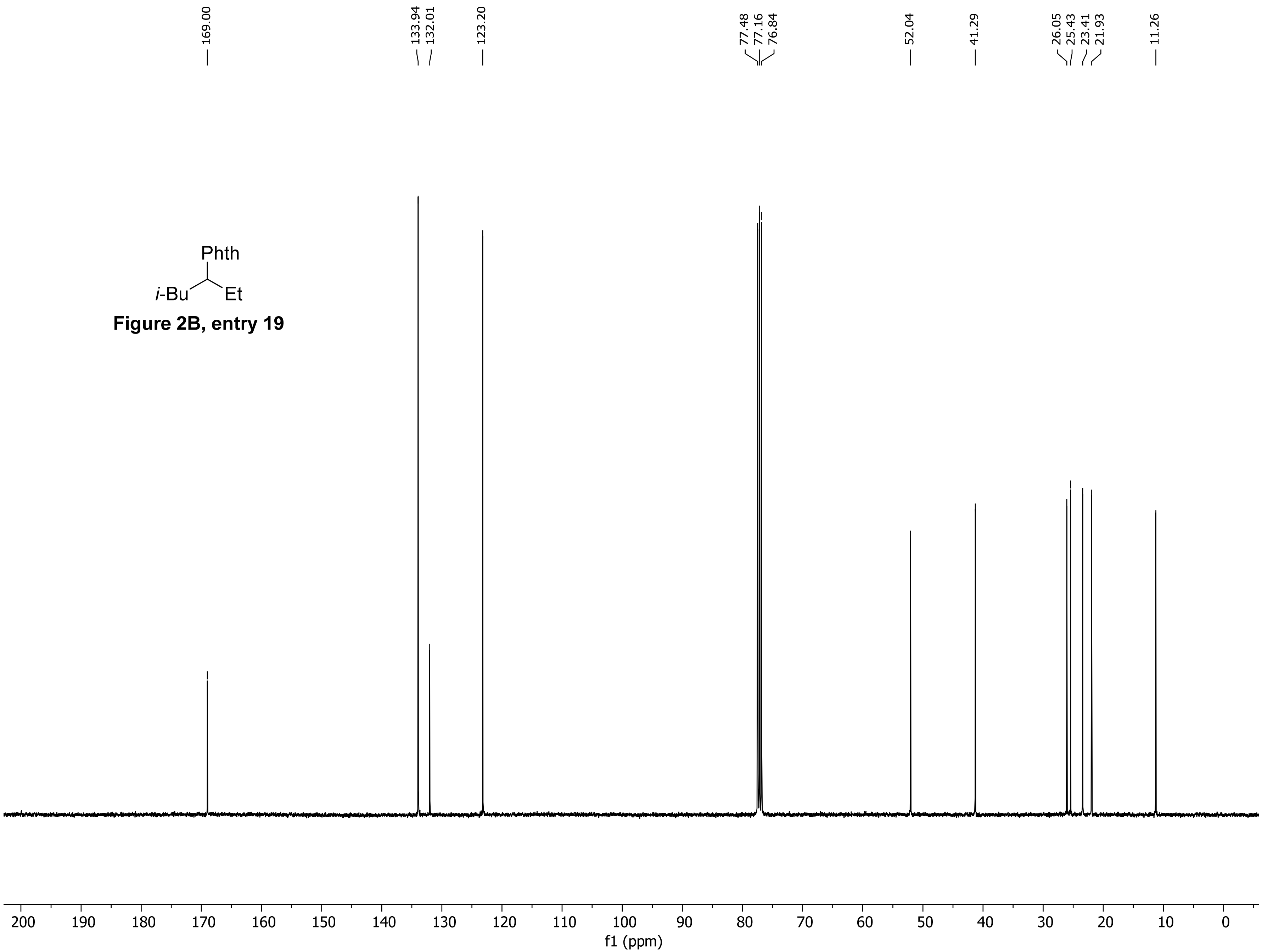


Figure 2B, entry 19

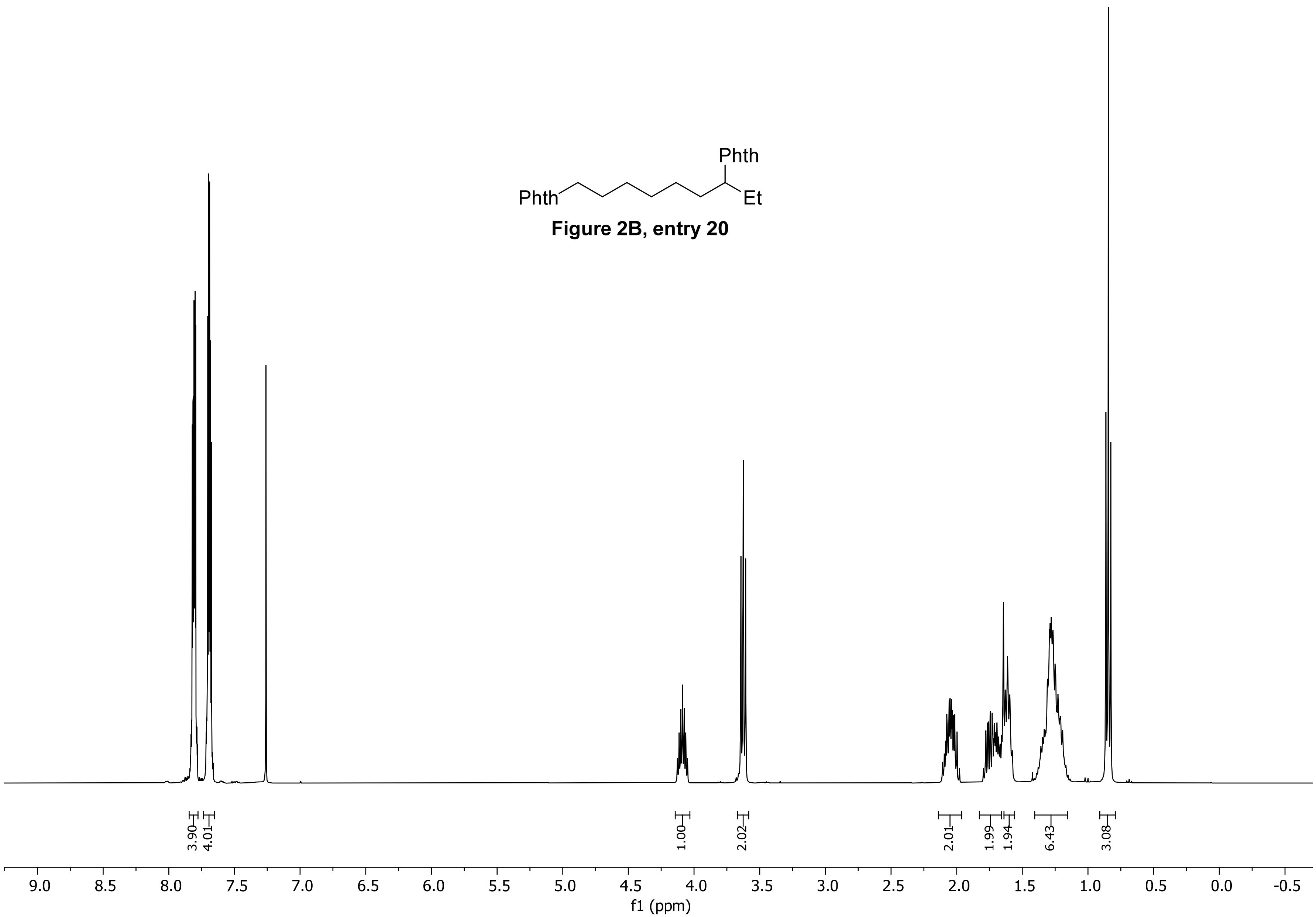


Figure 2B, entry 20

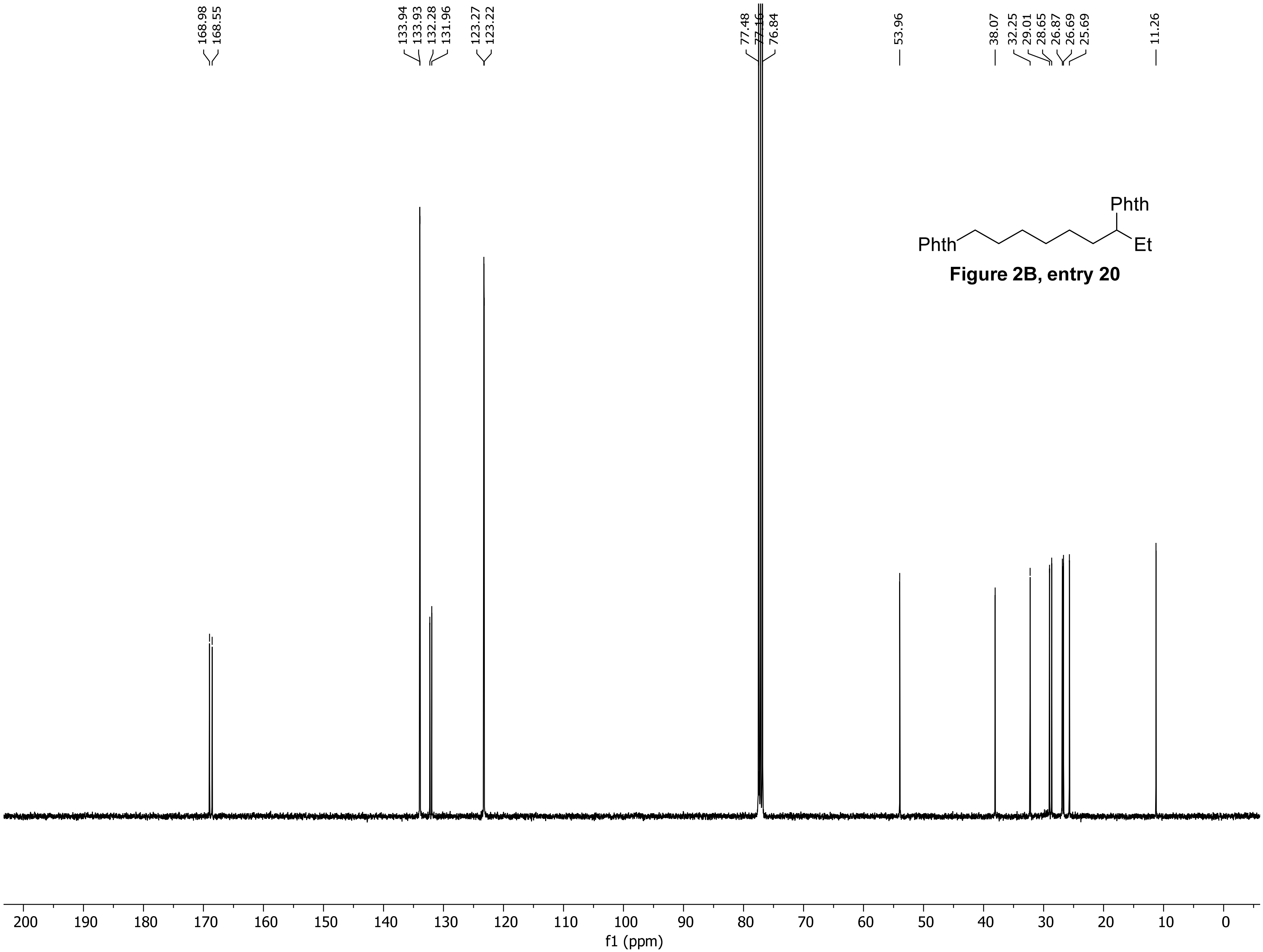


Figure 2B, entry 20

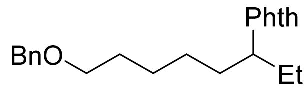
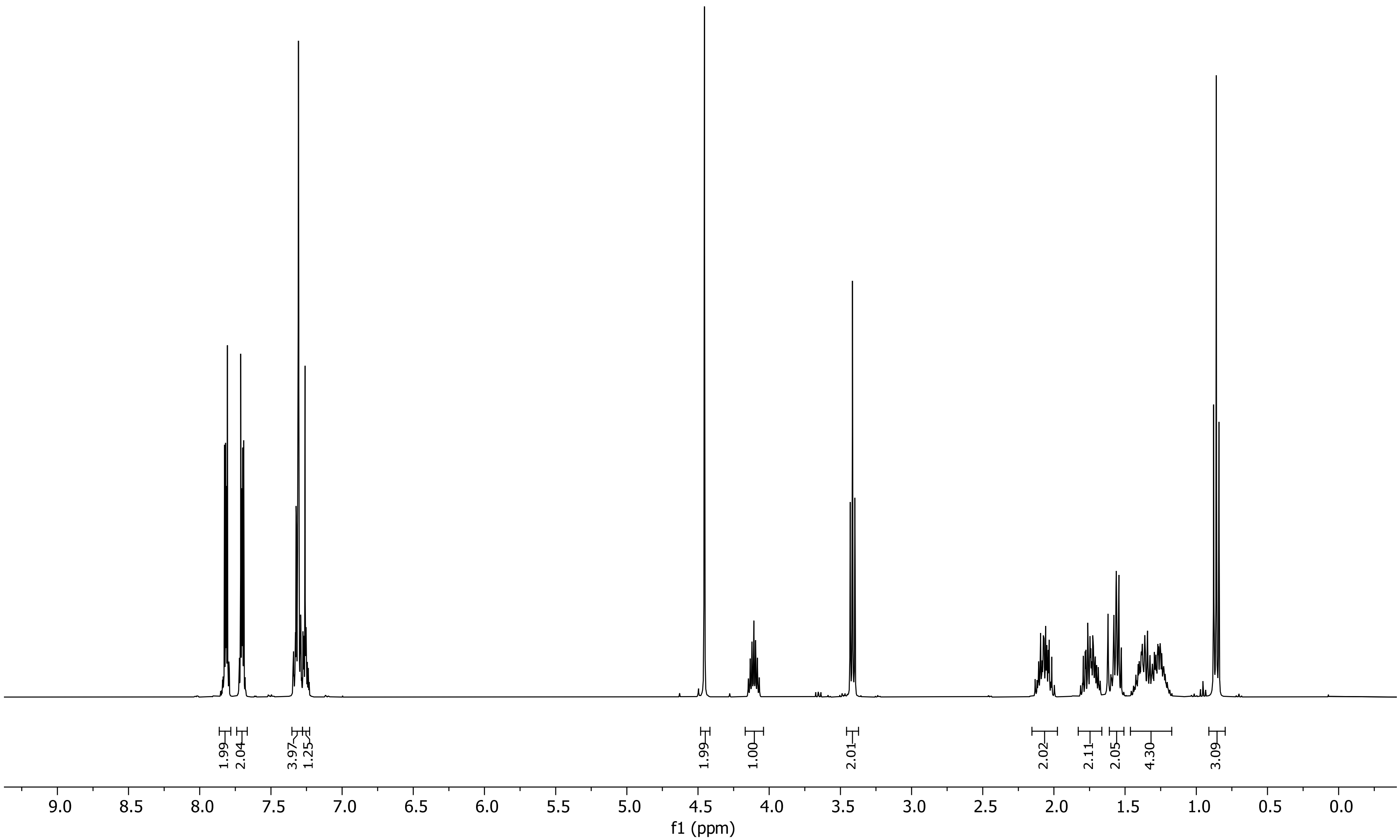
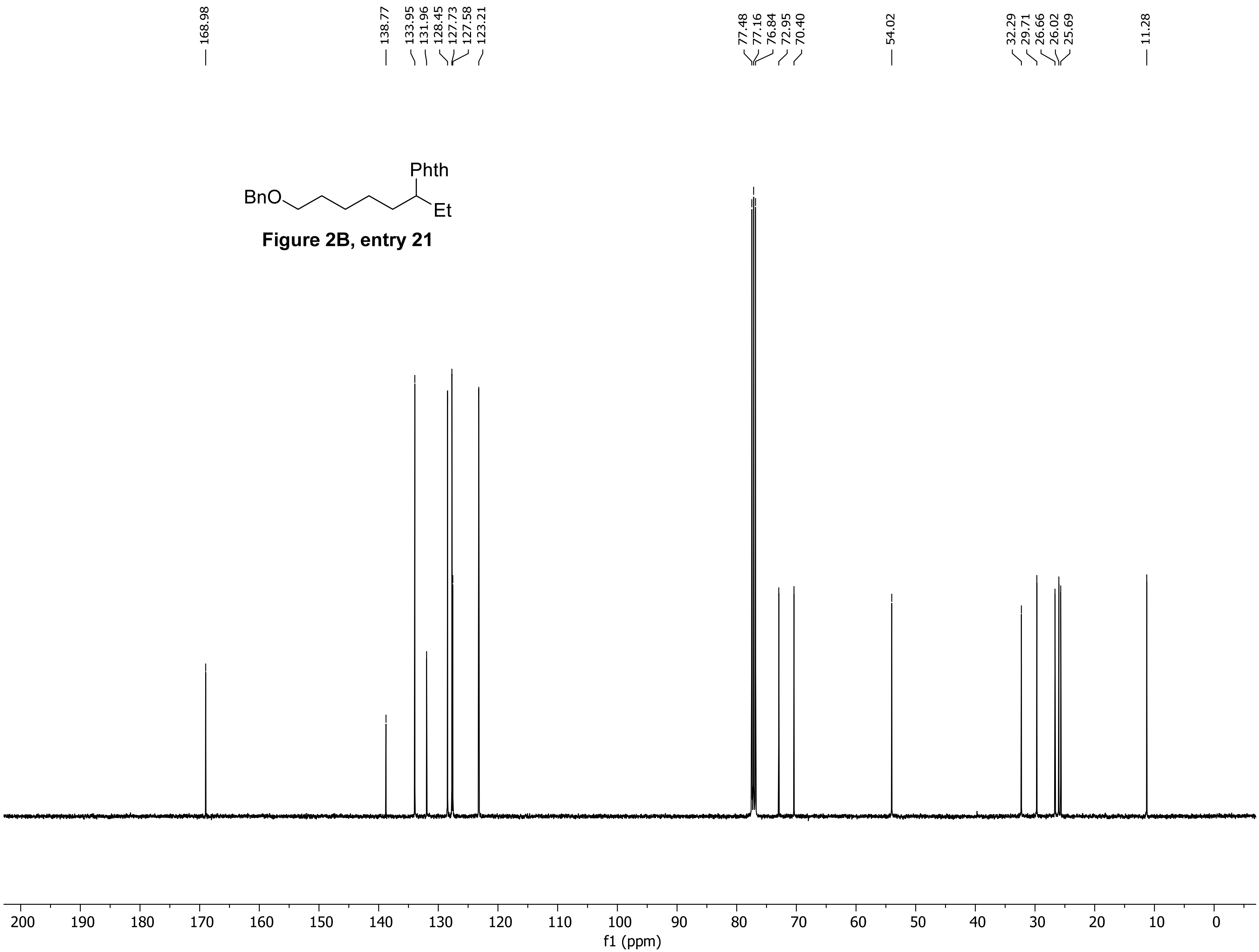
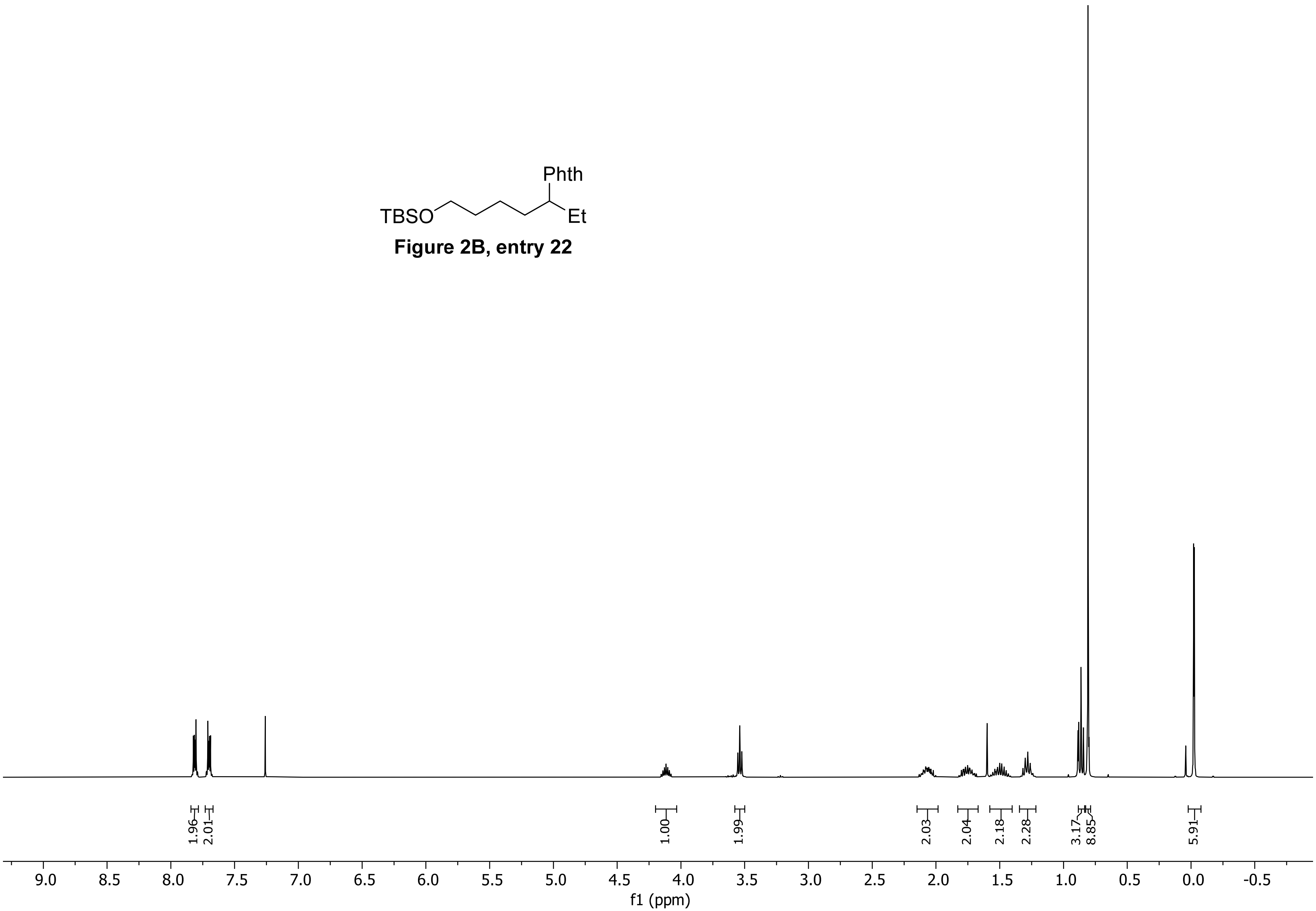


Figure 2B, entry 21




168.98
138.77
133.95
131.96
128.45
127.73
127.58
123.21
77.48
77.16
76.84
72.95
70.40
54.02
32.29
29.71
26.66
26.02
25.69
11.28
Phth
BnO
Et
Figure 2B, entry 21
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Phth
TBSO
Et
Figure 2B, entry 22
1.96
2.01
1.00
1.99
2.03
2.04
2.18
2.28
3.17
8.85
5.91
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

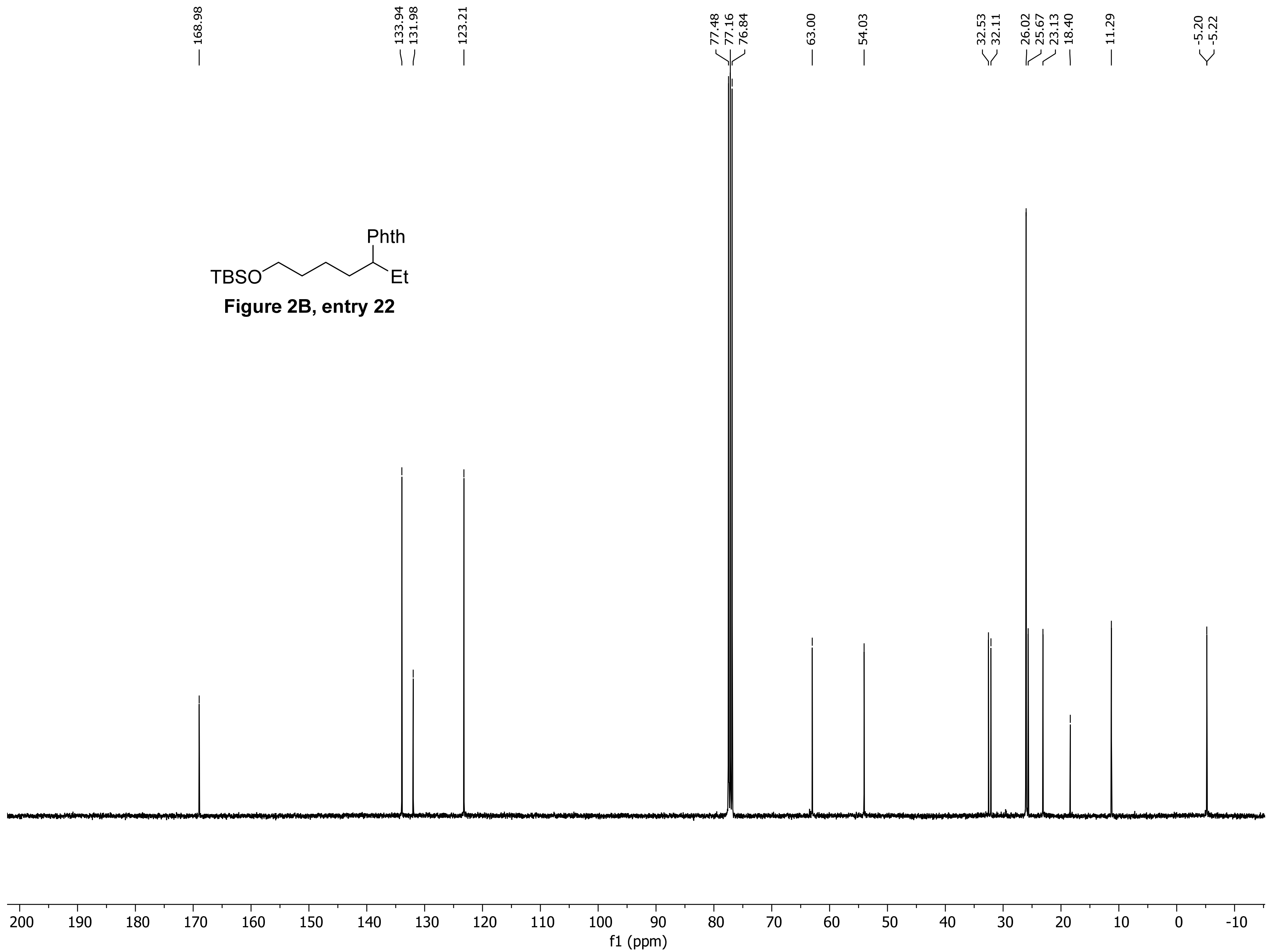


Figure 2B, entry 22

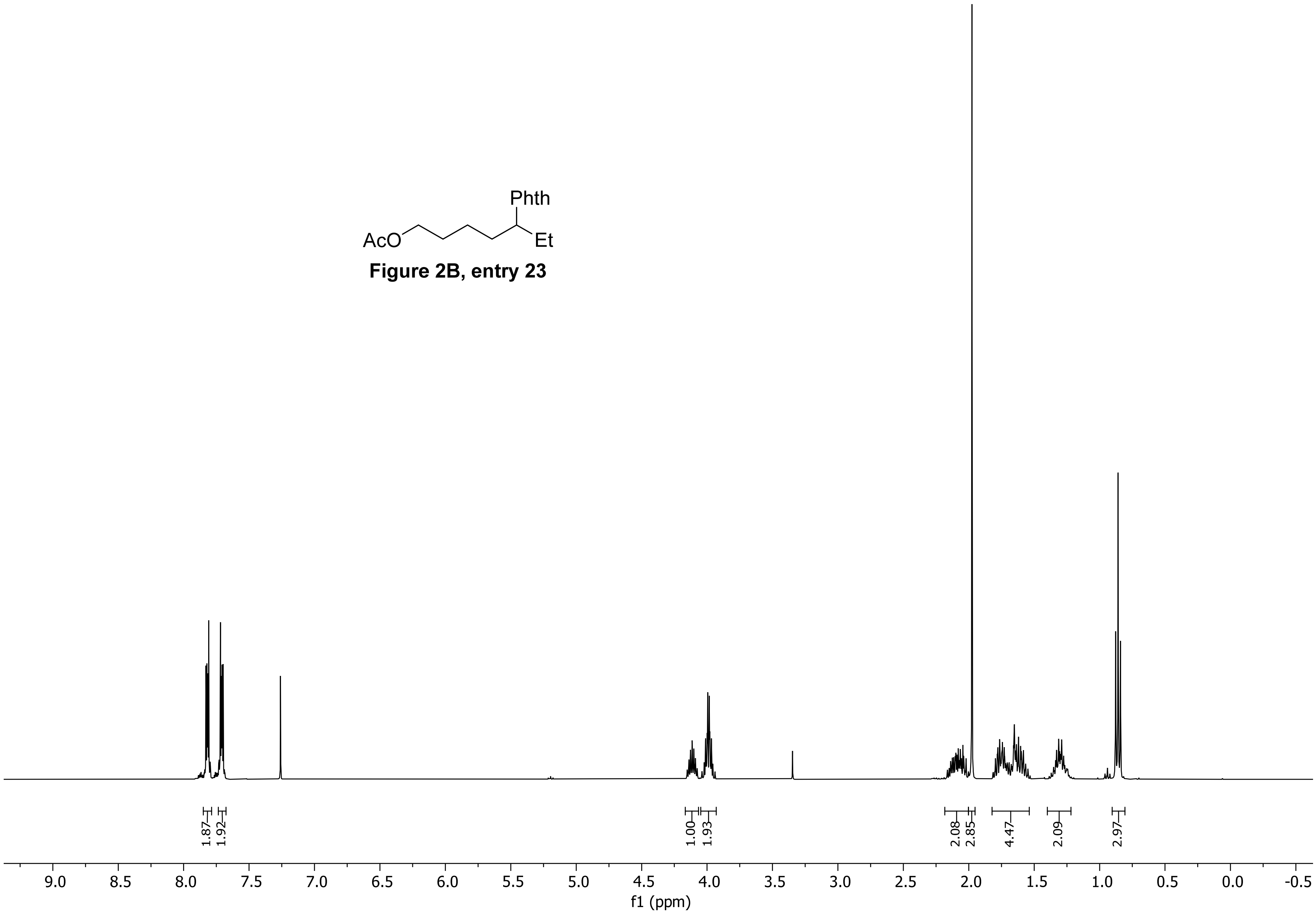
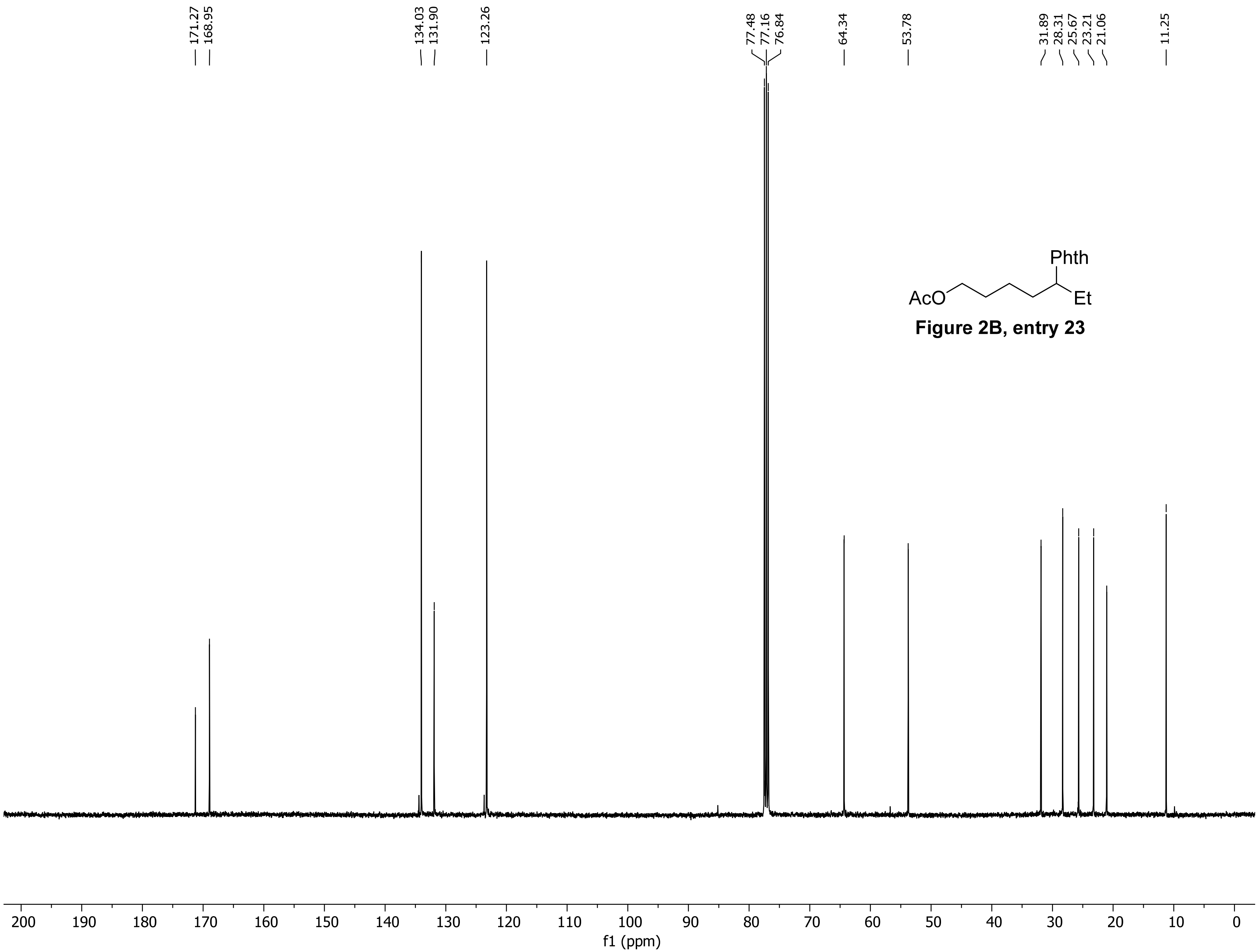
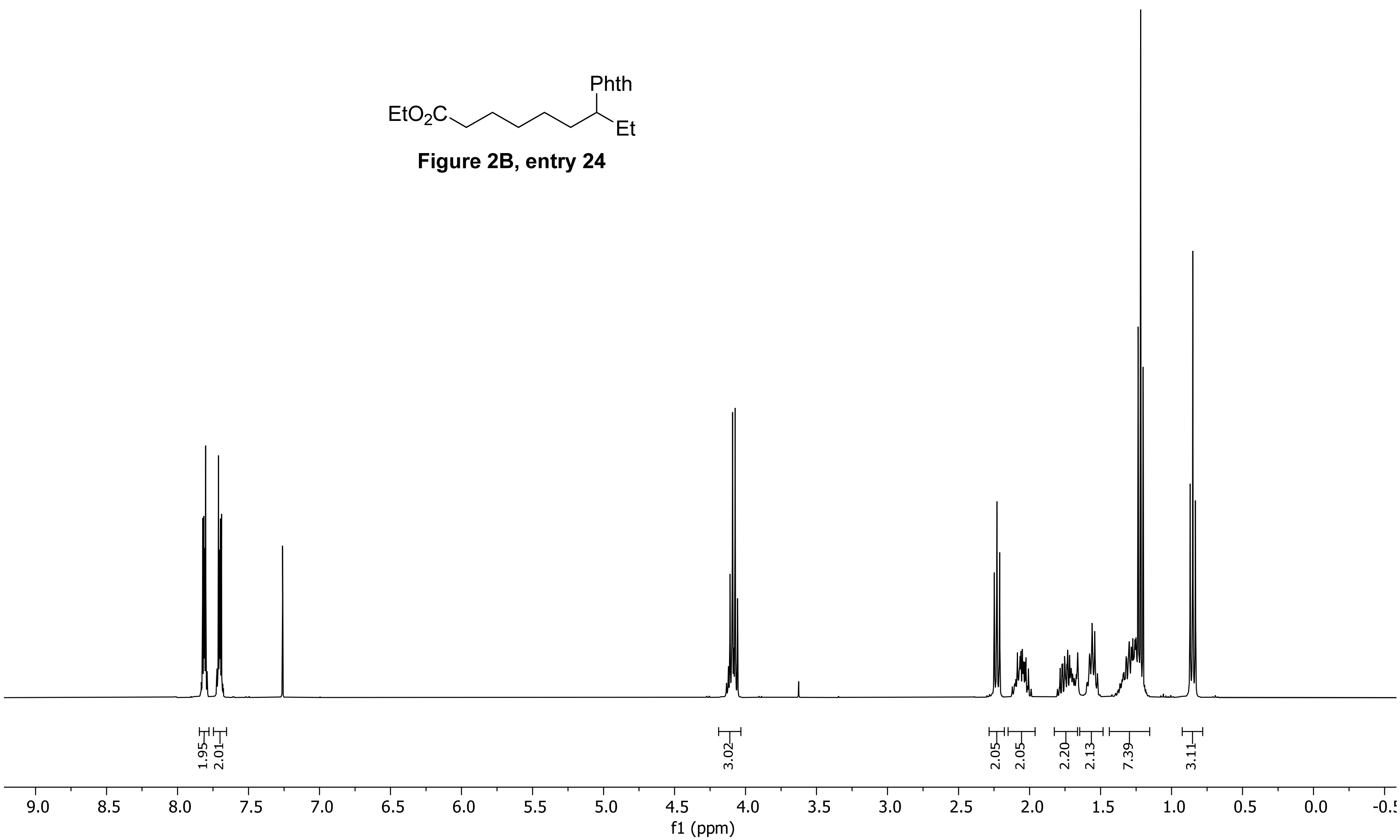
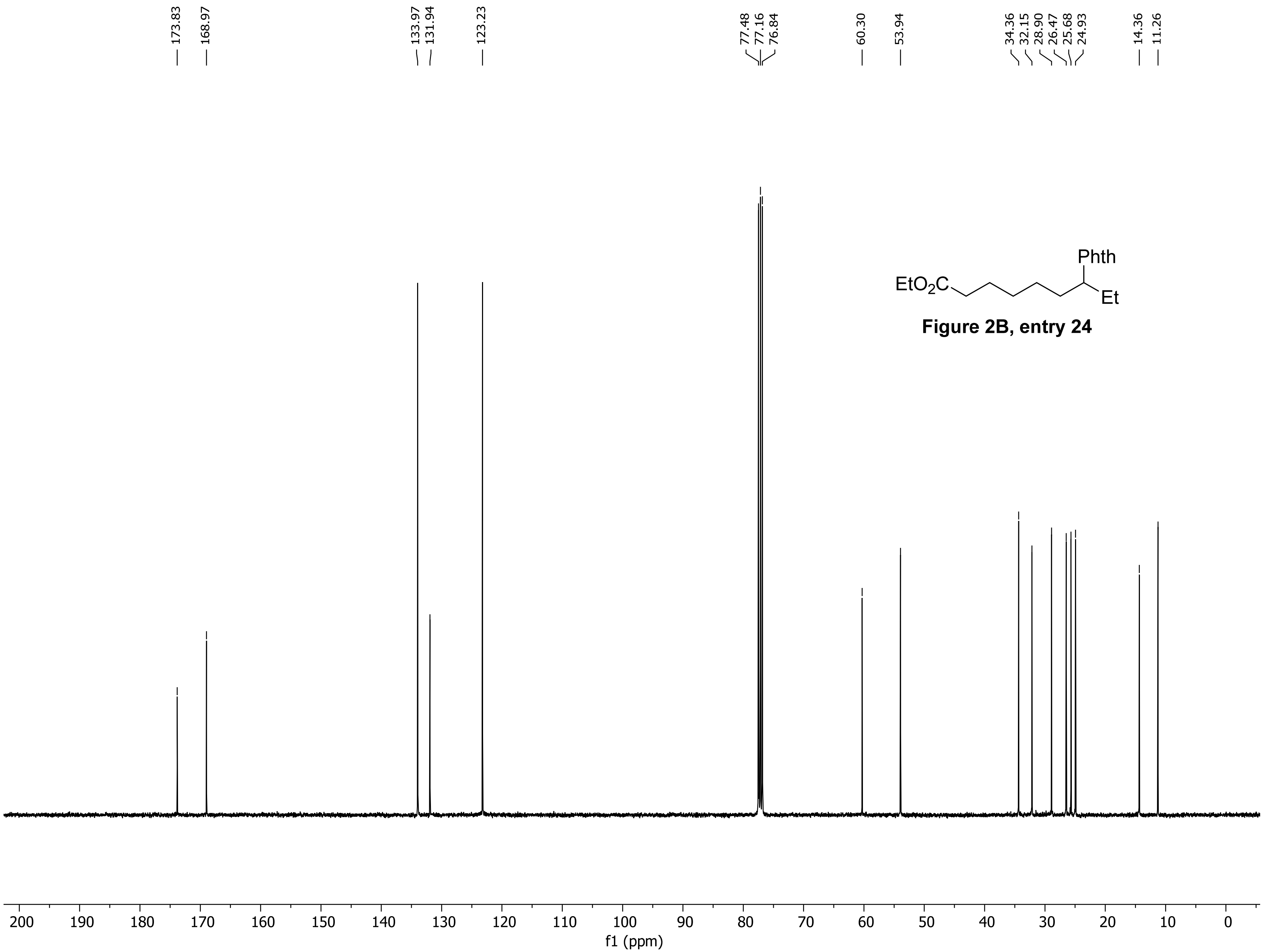
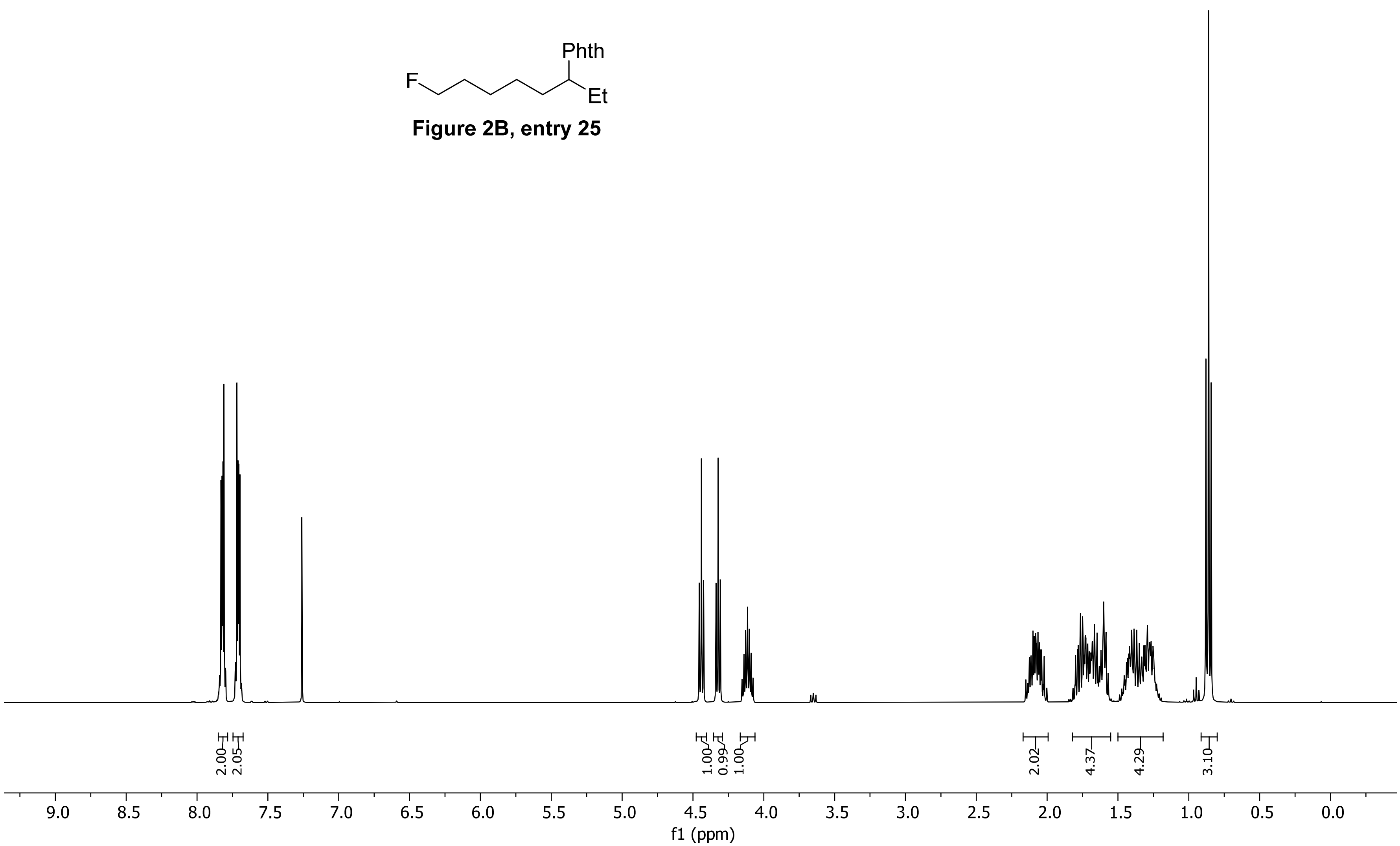


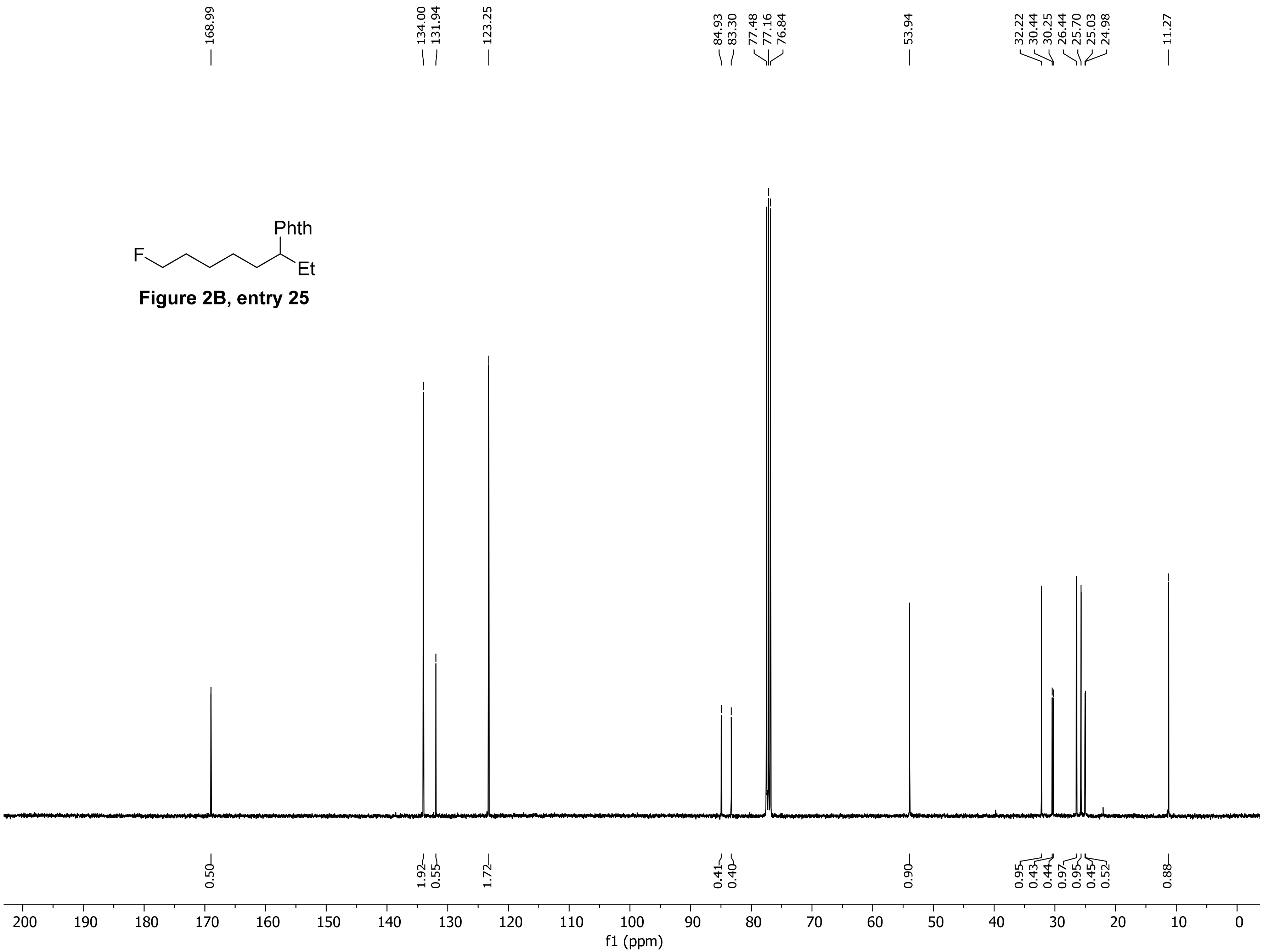
Figure 2B, entry 23

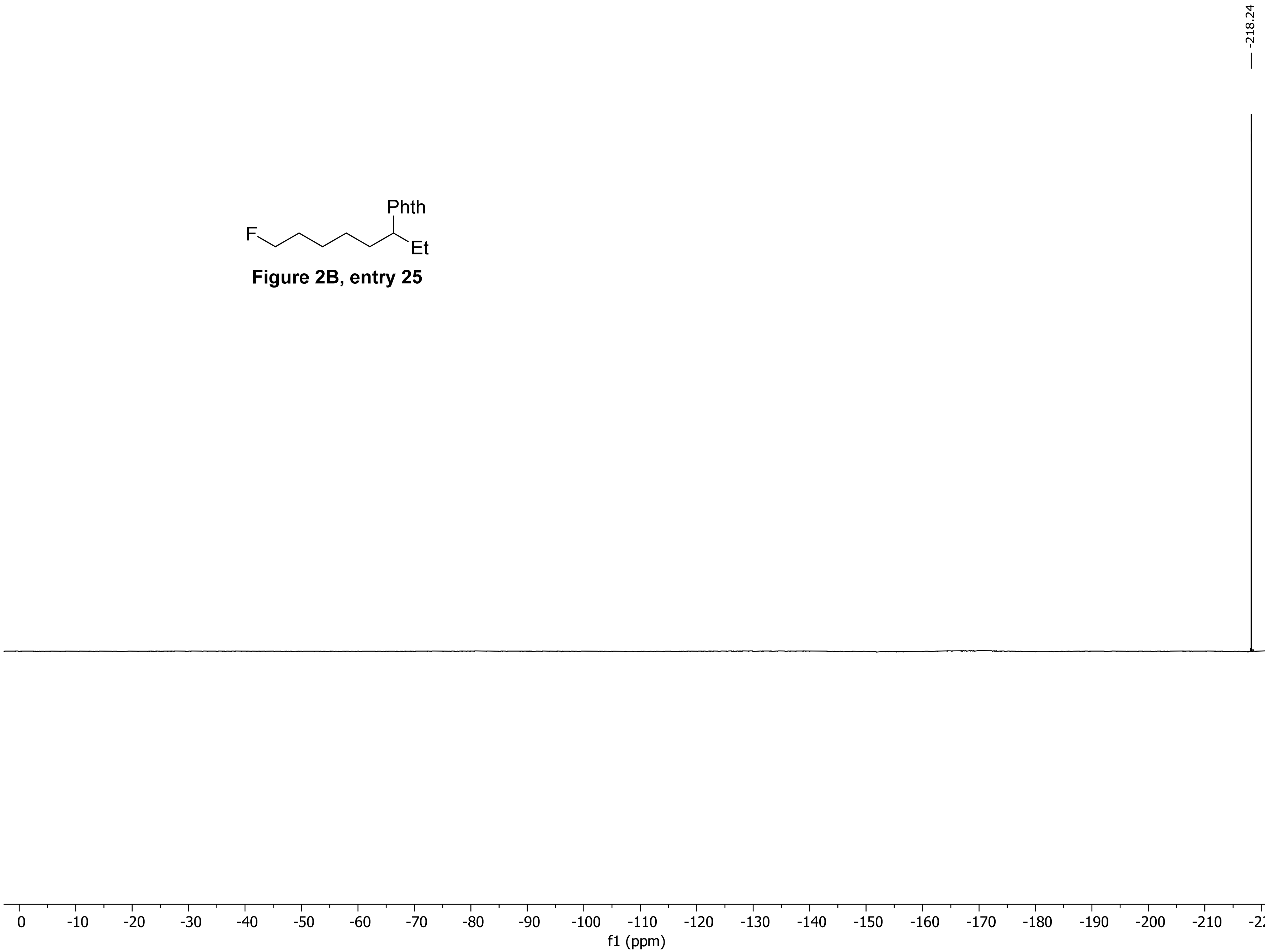

171.27
168.95
134.03
131.90
123.26
77.48
77.16
76.84
64.34
53.78
31.89
28.31
25.67
23.21
21.06
11.25
Phth
AcO
Et
Figure 2B, entry 23
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Phth
EtO2C
Et
Figure 2B, entry 24
1.95
2.01
3.02
2.05
2.05
2.20
2.13
7.39
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.83
168.97
133.97
131.94
123.23
77.48
77.16
76.84
60.30
53.94
34.36
32.15
28.90
26.47
25.68
24.93
14.36
11.26
Phth
EtO2C
Et
Figure 2B, entry 24
f1 (ppm)


Phth
F
Et
Figure 2B, entry 25
2.00
2.05
1.00
0.99
1.00
2.02
4.37
4.29
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.99
134.00
131.94
123.25
84.93
83.30
77.48
77.16
76.84
53.94
32.22
30.44
30.25
26.44
25.70
25.03
24.98
11.27
F
Phth
Et
Figure 2B, entry 25
0.50
1.92
0.55
1.72
0.41
0.40
0.90
0.95
0.43
0.44
0.97
0.95
0.45
0.52
0.88
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


F
Phth
Et
Figure 2B, entry 25
-218.24
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

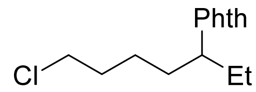
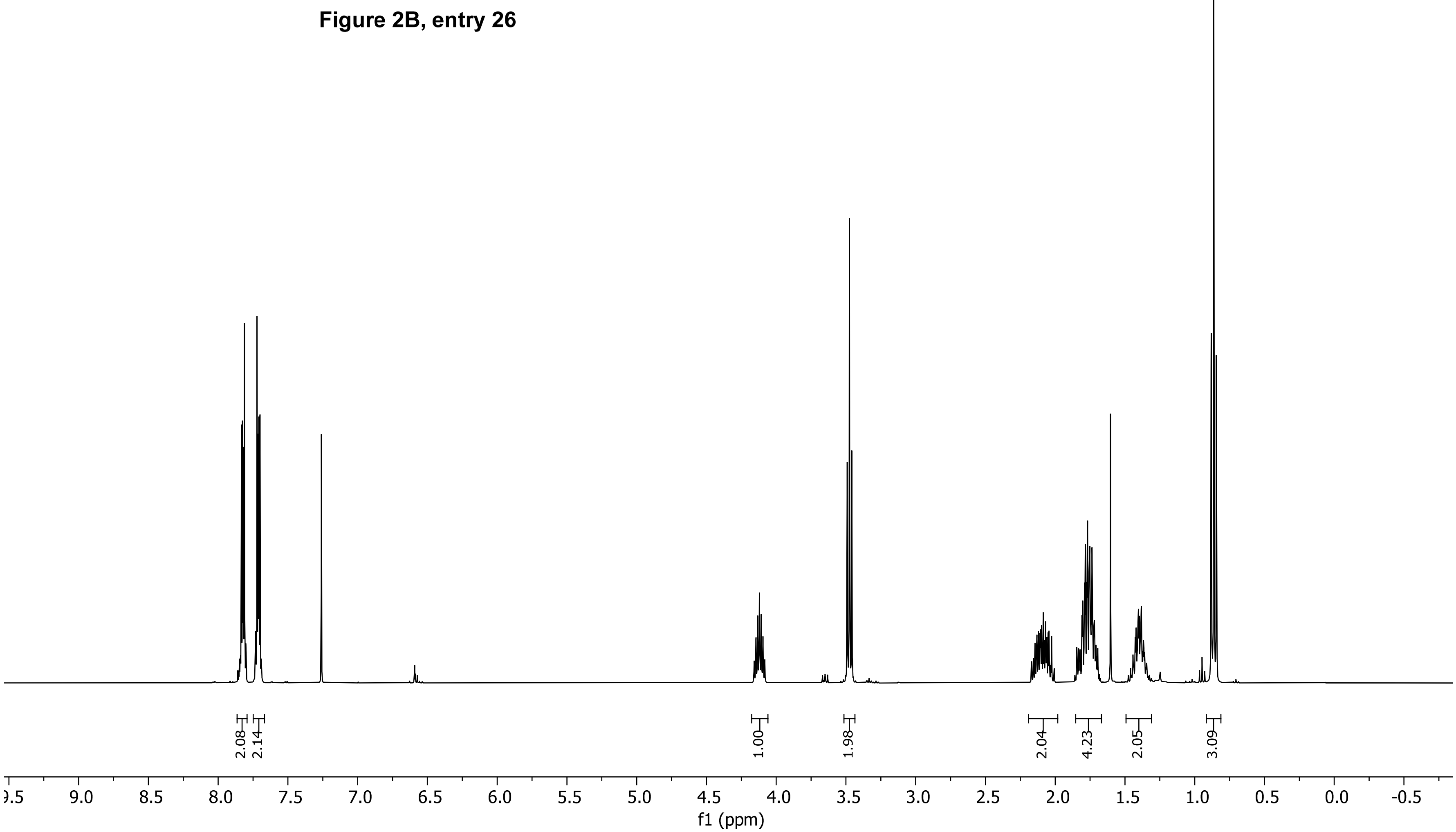
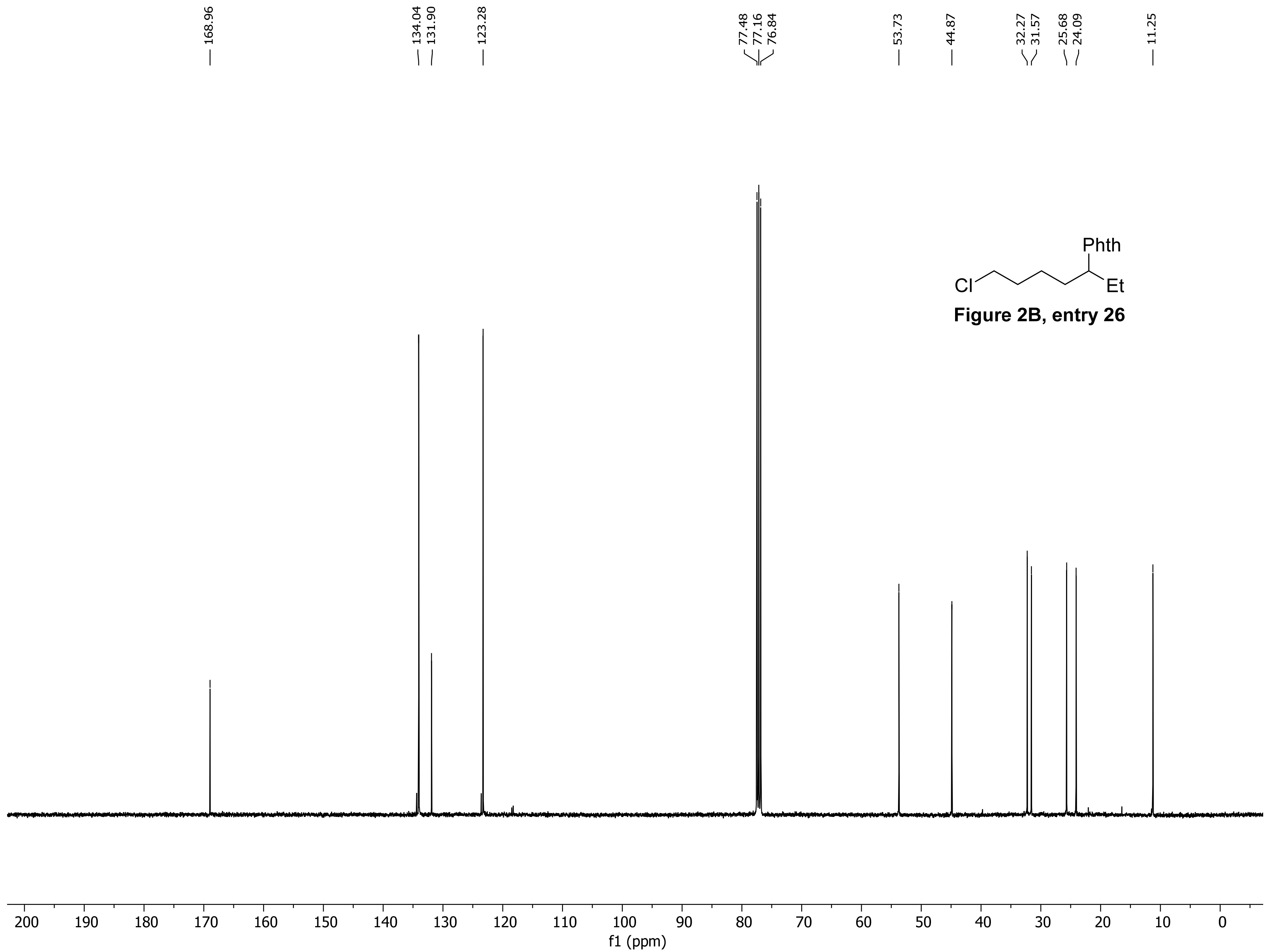


Figure 2B, entry 26




168.96
134.04
131.90
123.28
77.48
77.16
76.84
53.73
44.87
32.27
31.57
25.68
24.09
11.25
Phth
Cl
Et
Figure 2B, entry 26
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

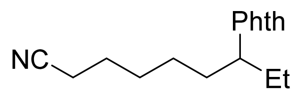
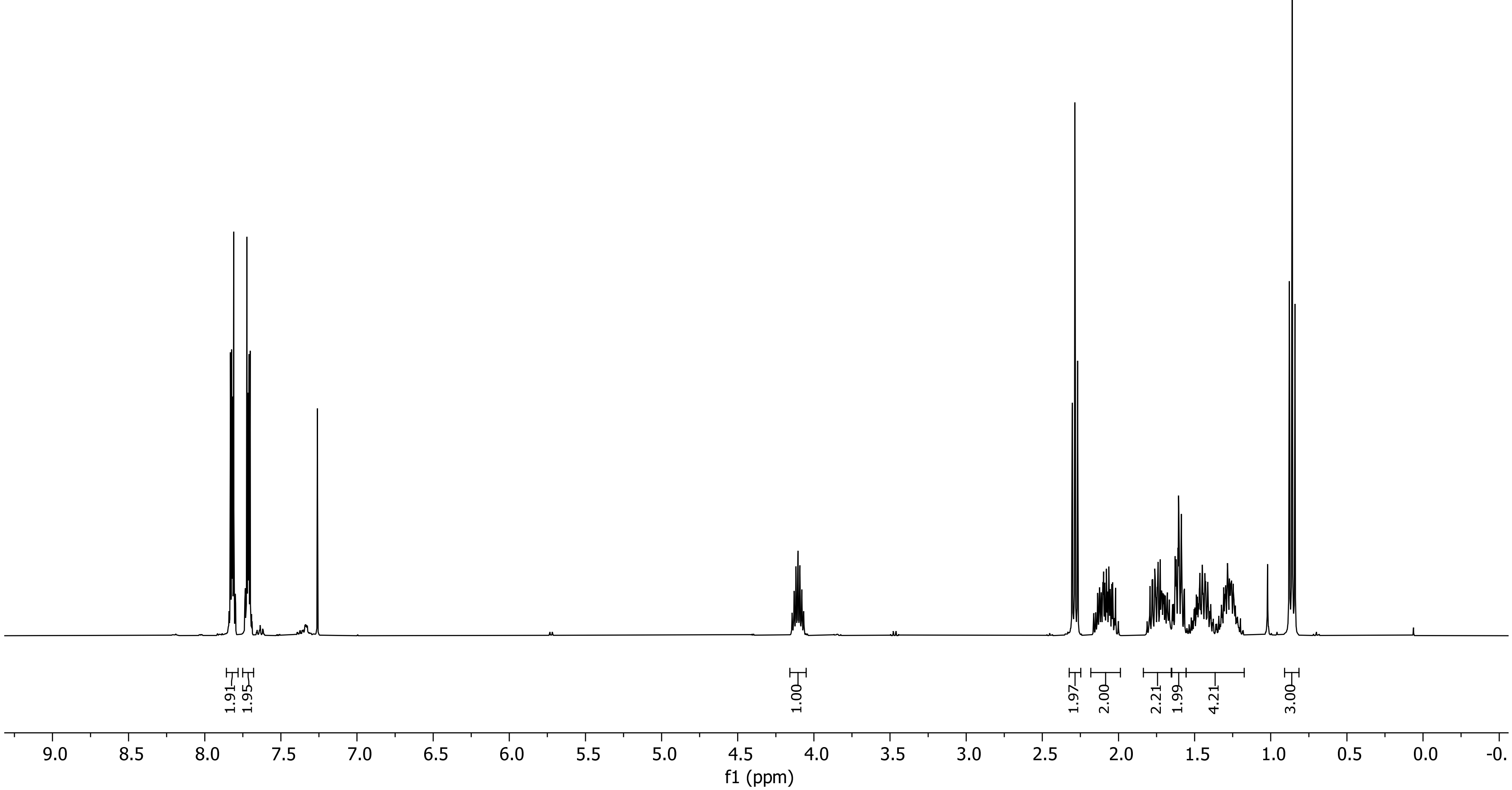


Figure 2B, entry 27



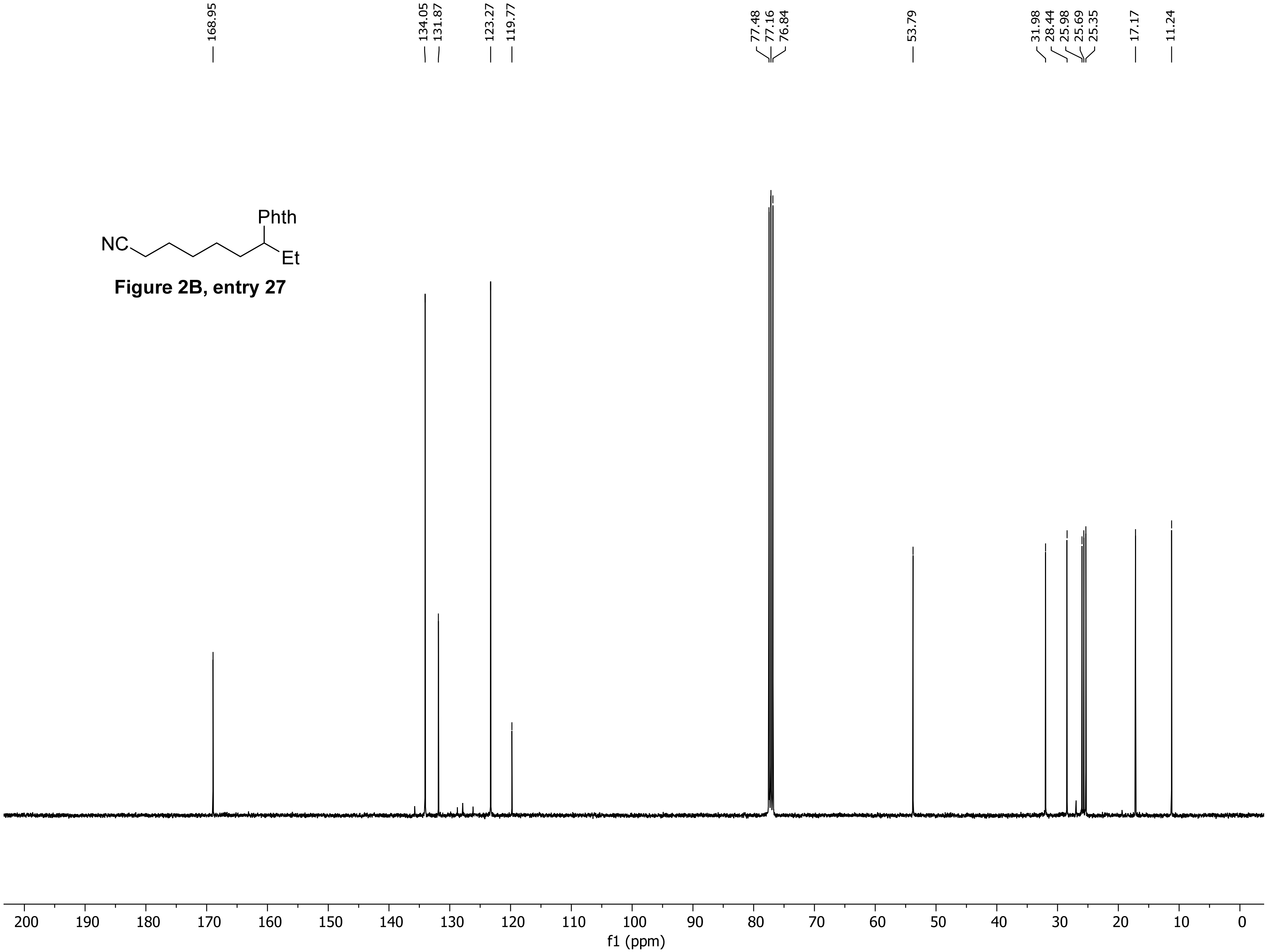


Figure 2B, entry 27

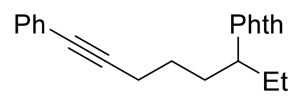
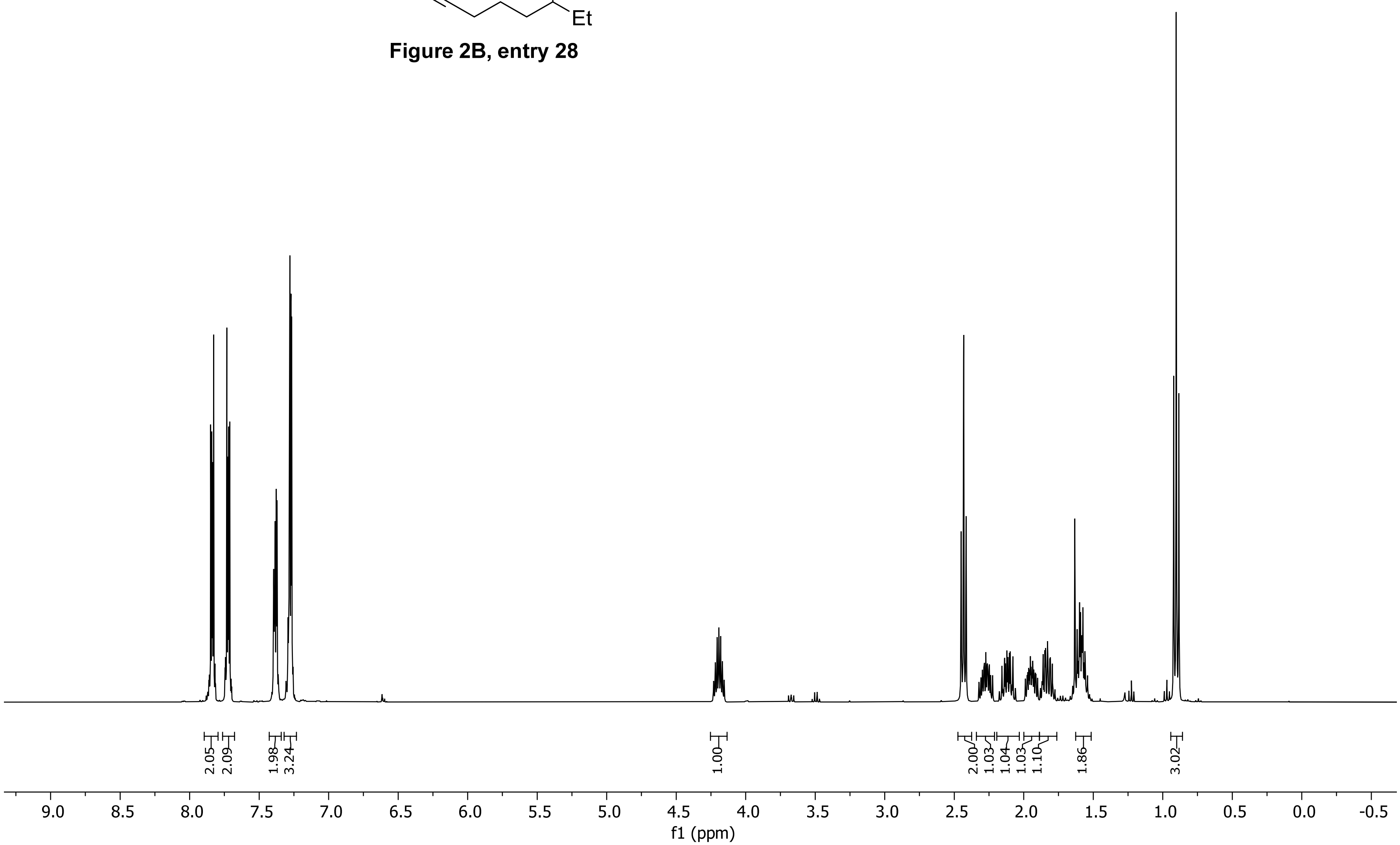
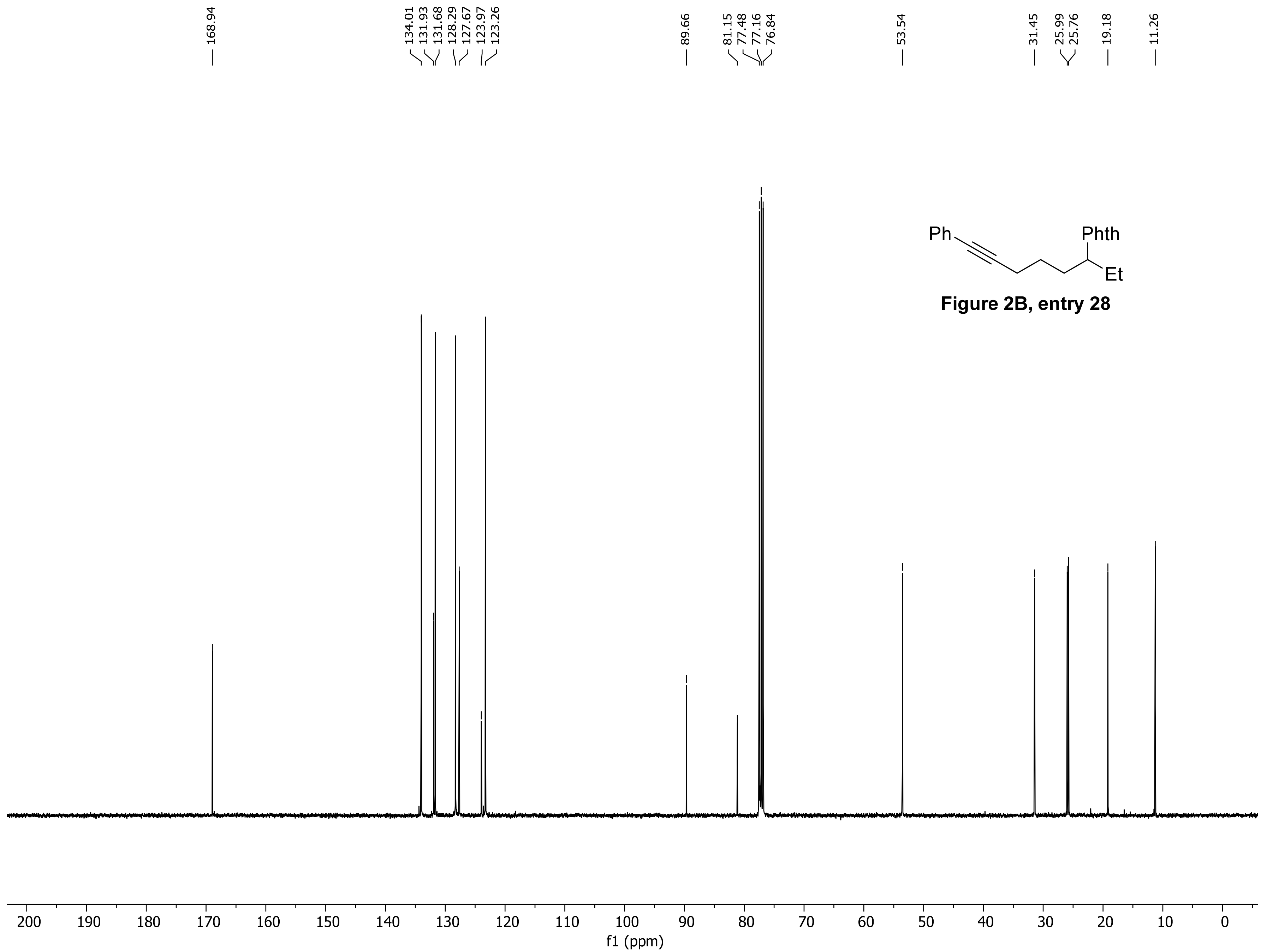


Figure 2B, entry 28




168.94
134.01
131.93
131.68
128.29
127.67
123.97
123.26
89.66
81.15
77.48
77.16
76.84
53.54
31.45
25.99
25.76
19.18
11.26
Ph
Phth
Et
Figure 2B, entry 28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

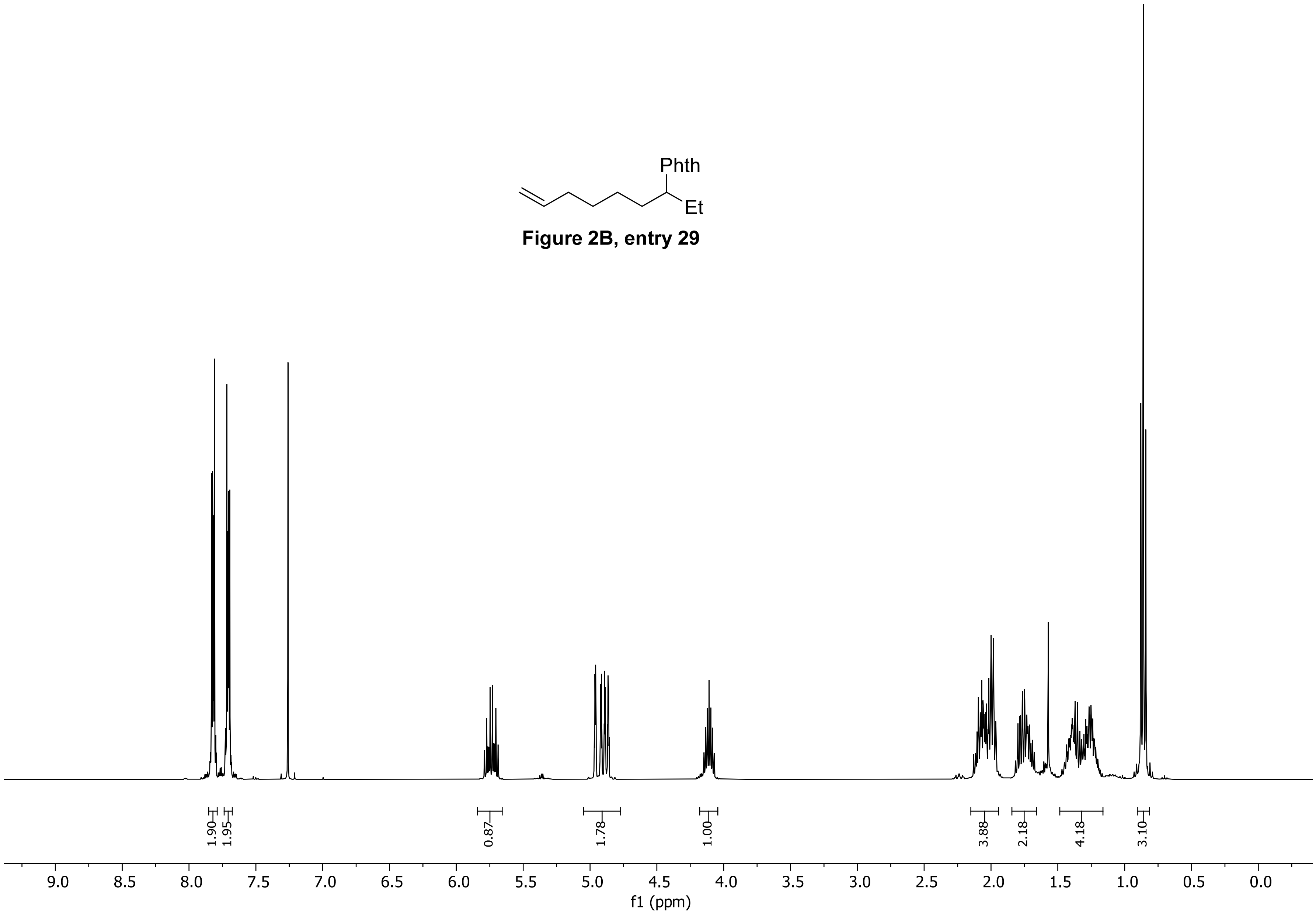
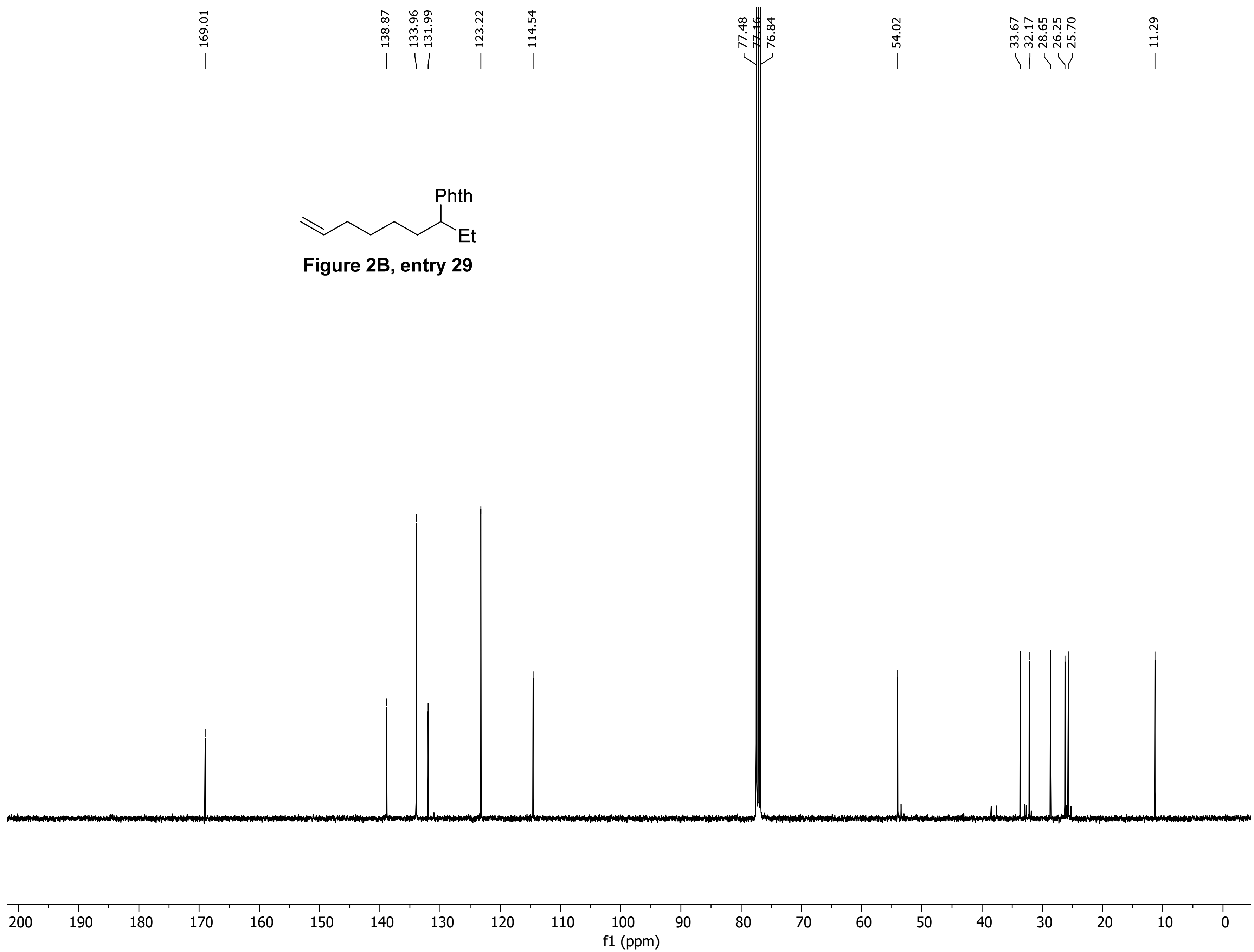


Figure 2B, entry 29


169.01
138.87
133.96
131.99
123.22
114.54
77.48
77.16
76.84
54.02
33.67
32.17
28.65
26.25
25.70
11.29
Phth
Et
Figure 2B, entry 29
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

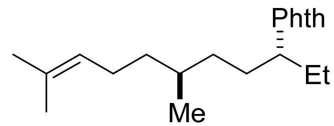
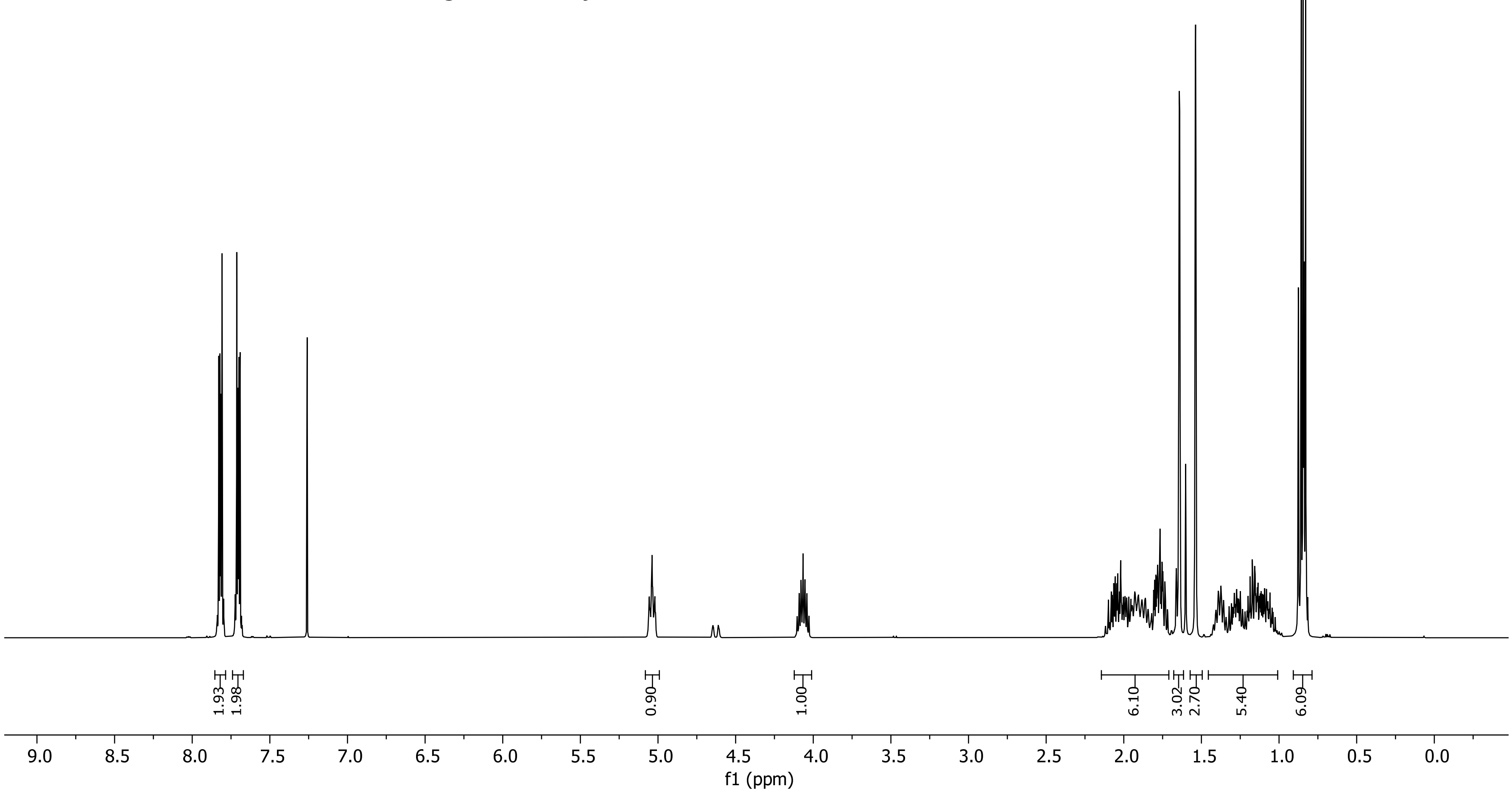


Figure 2B, entry 30



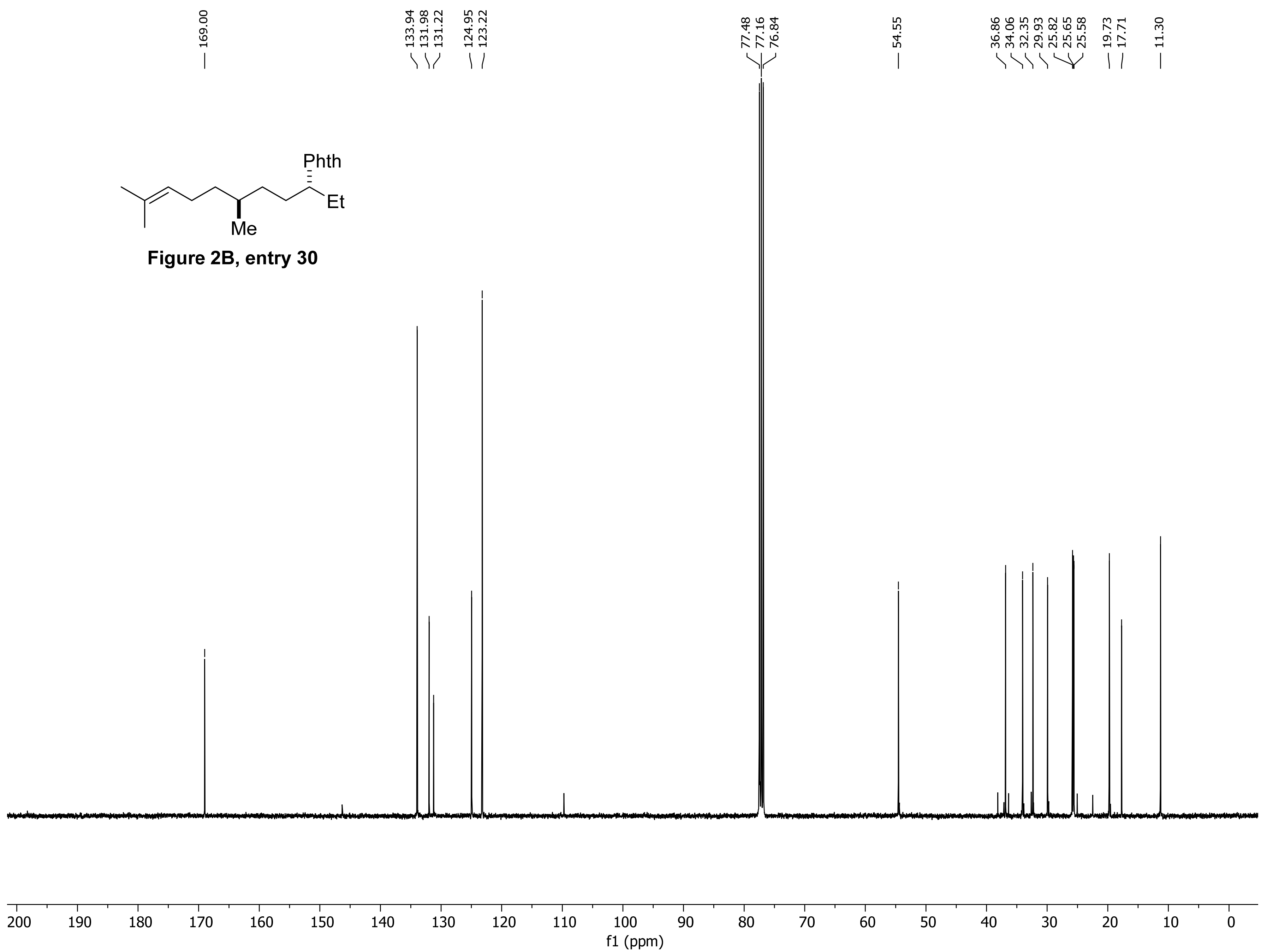


Figure 2B, entry 30

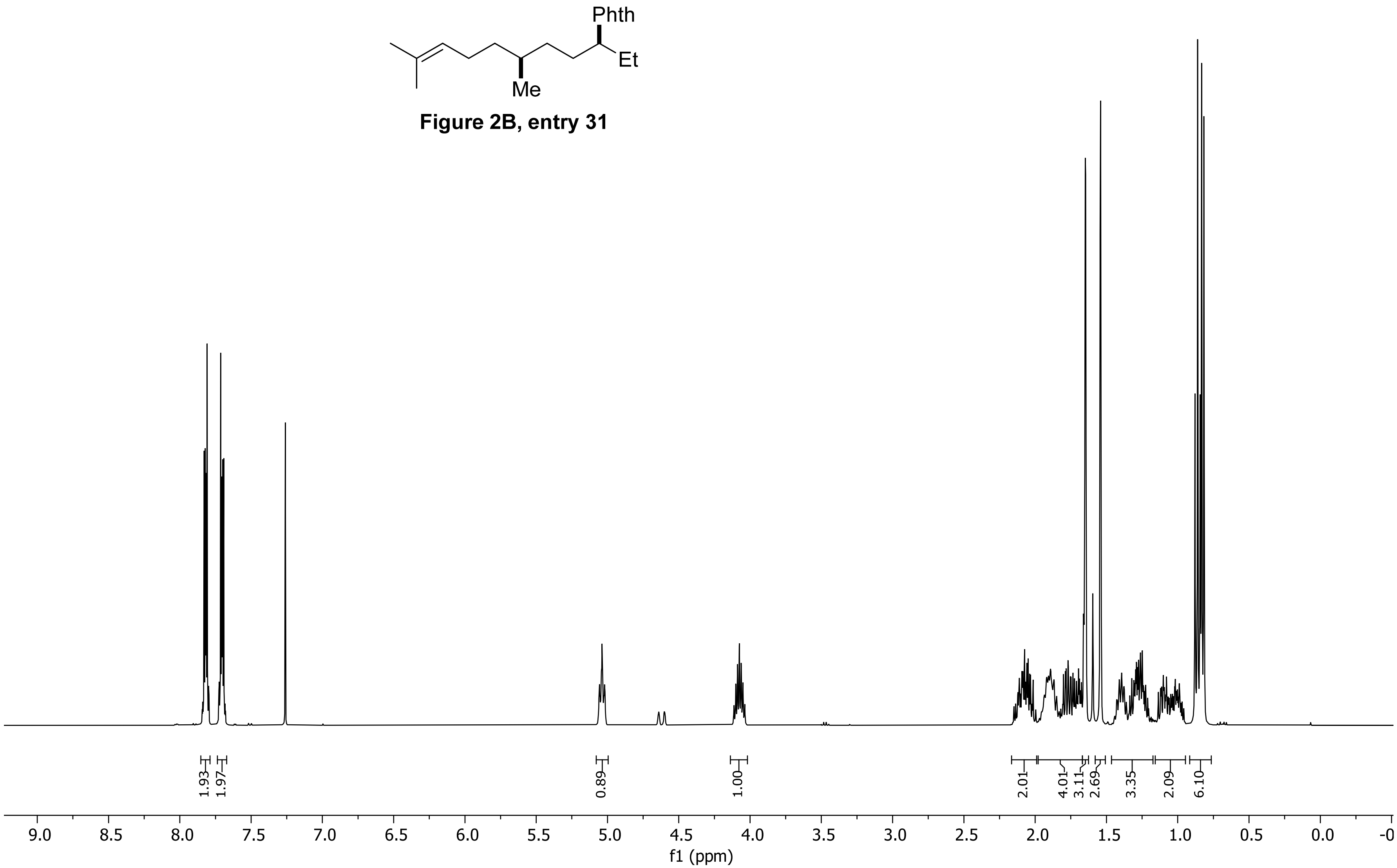


Figure 2B, entry 31

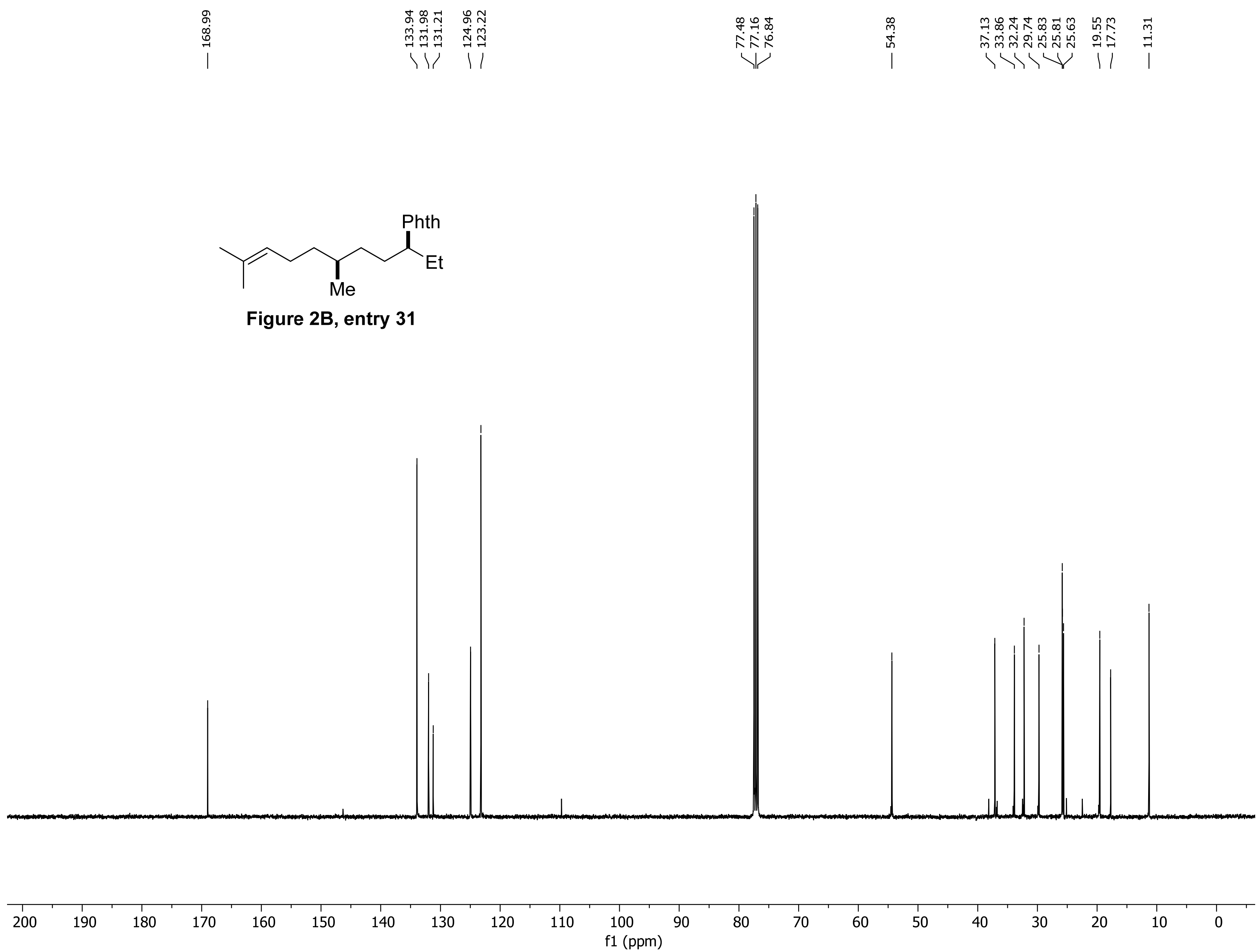


Figure 2B, entry 31

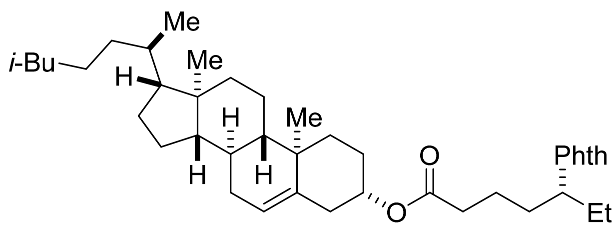
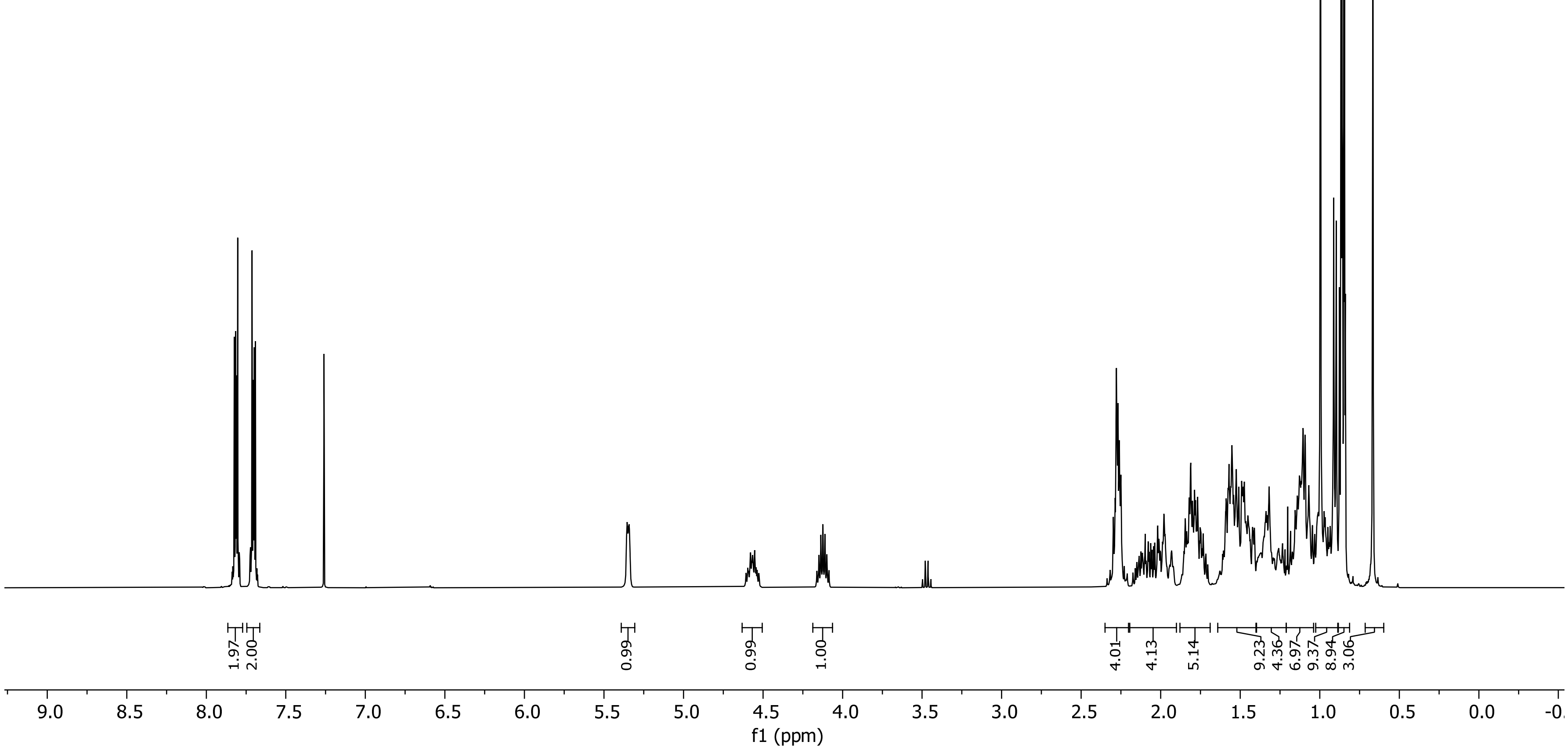


Figure 2B, entry 32



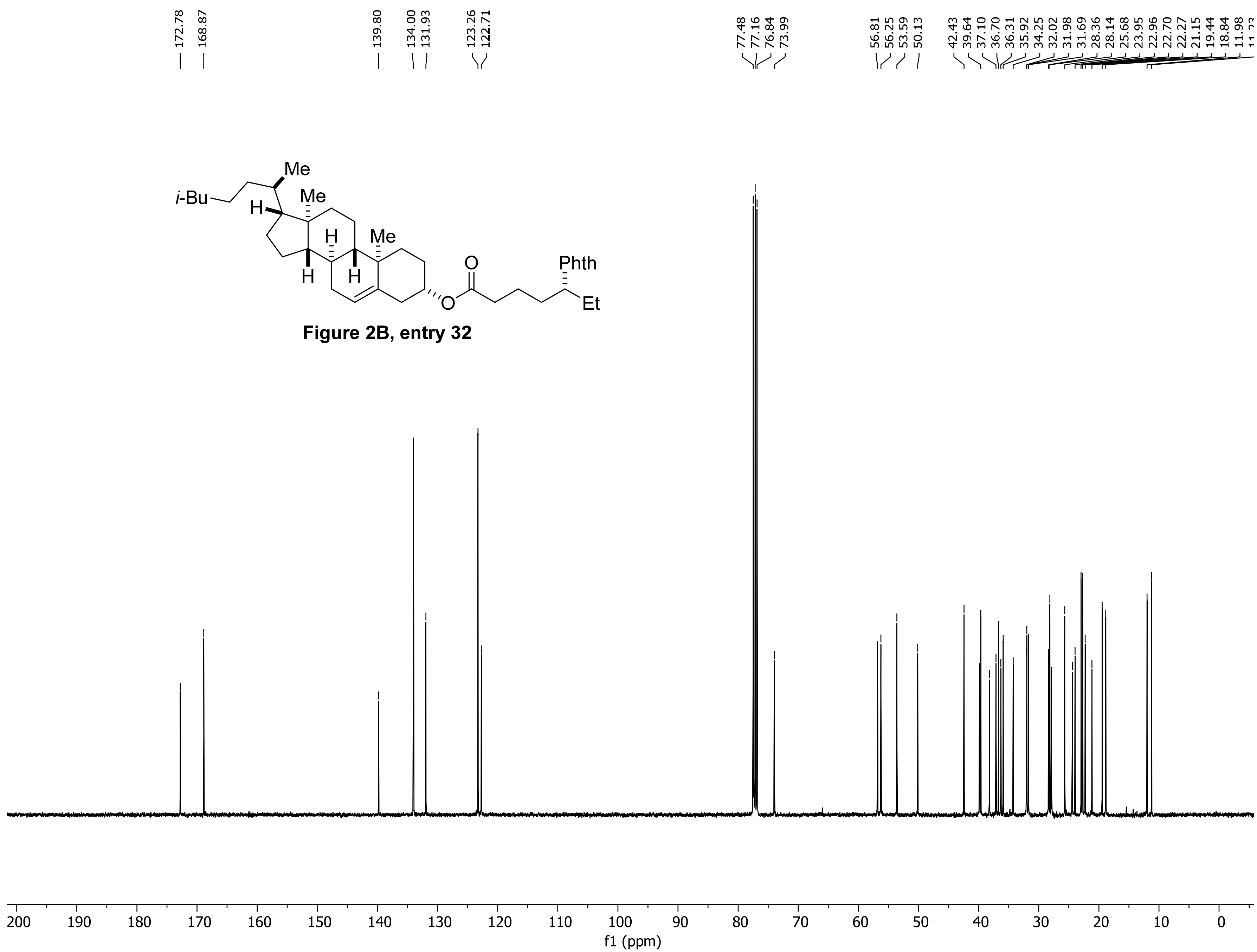
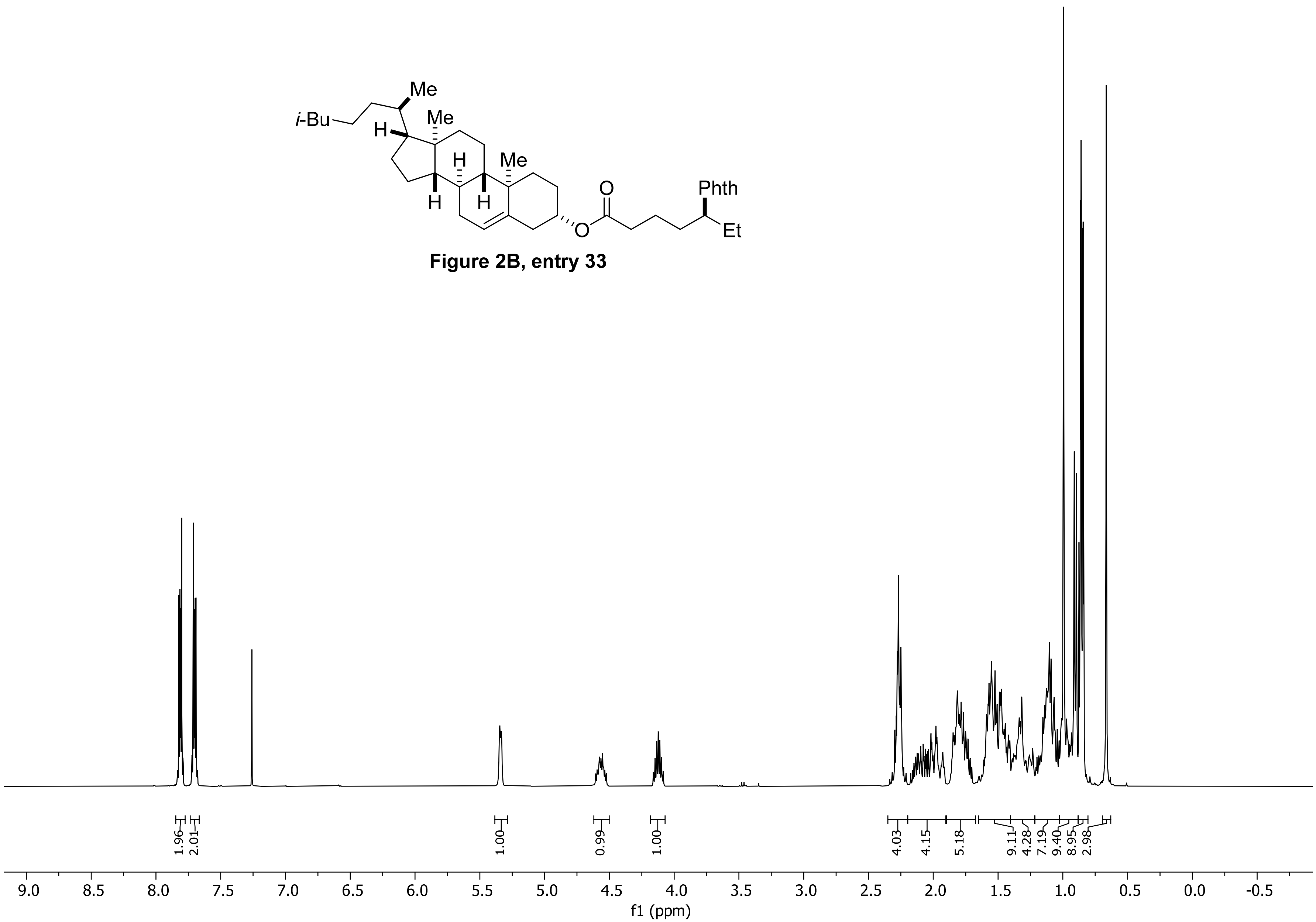


Figure 2B, entry 32


Me
Me
i-Bu
H
H
Me
H
H
O
Phth
O
Et
Figure 2B, entry 33
1.96
2.01
1.00
0.99
1.00
4.03
4.15
5.18
9.11
4.28
7.19
9.40
8.95
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

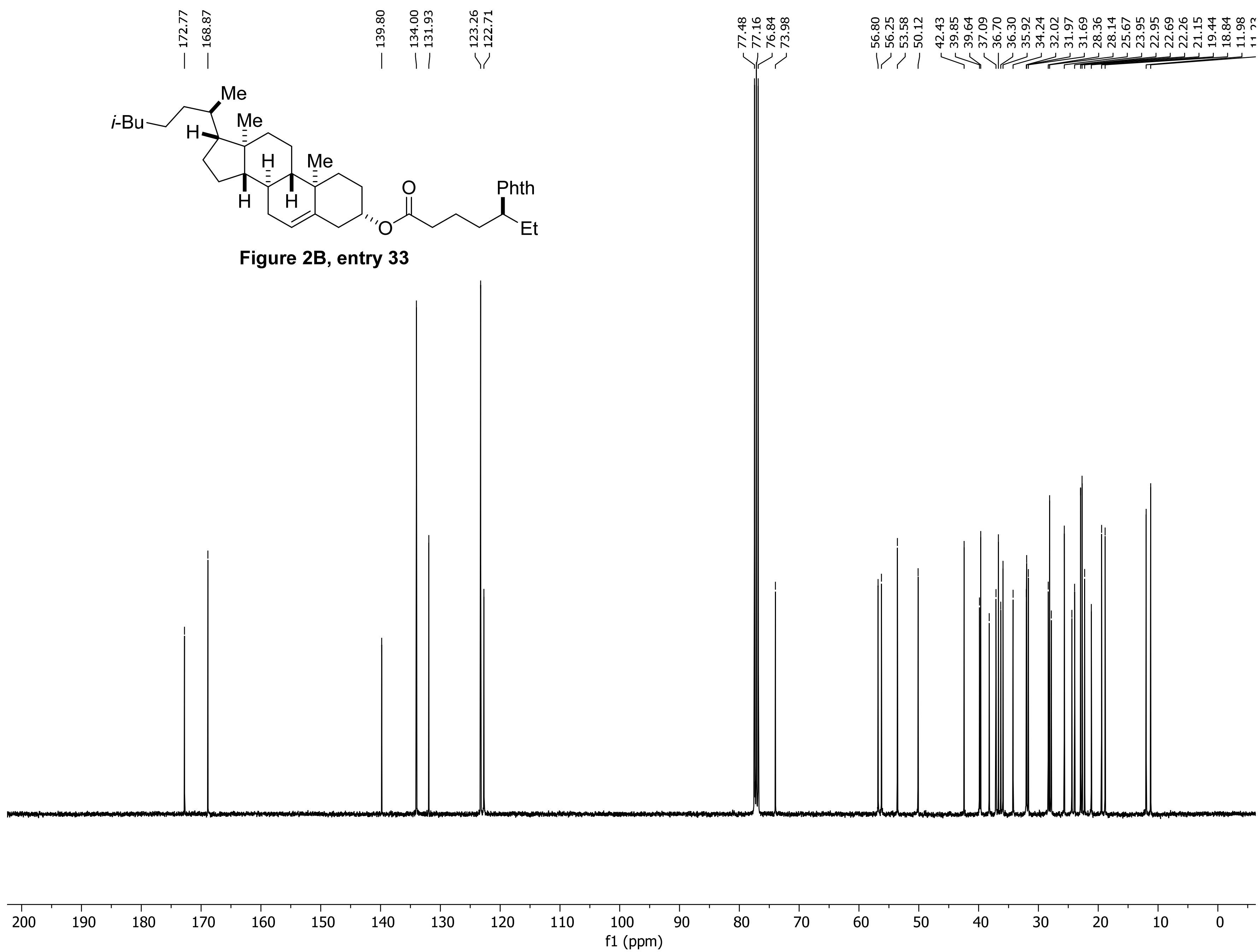


Figure 2B, entry 33

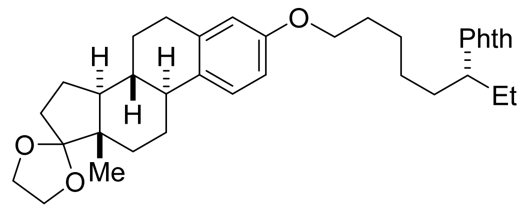
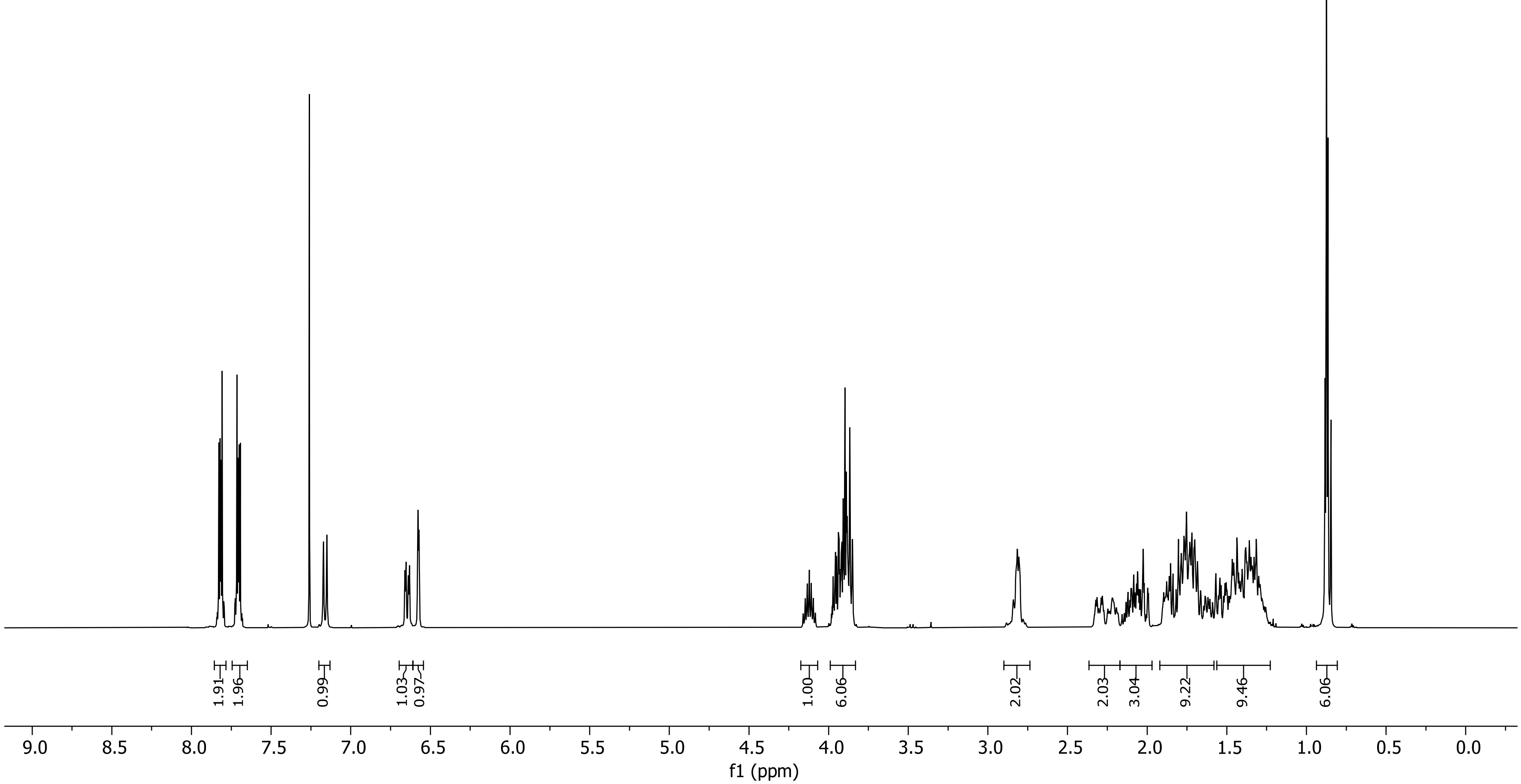


Figure 2B, entry 34



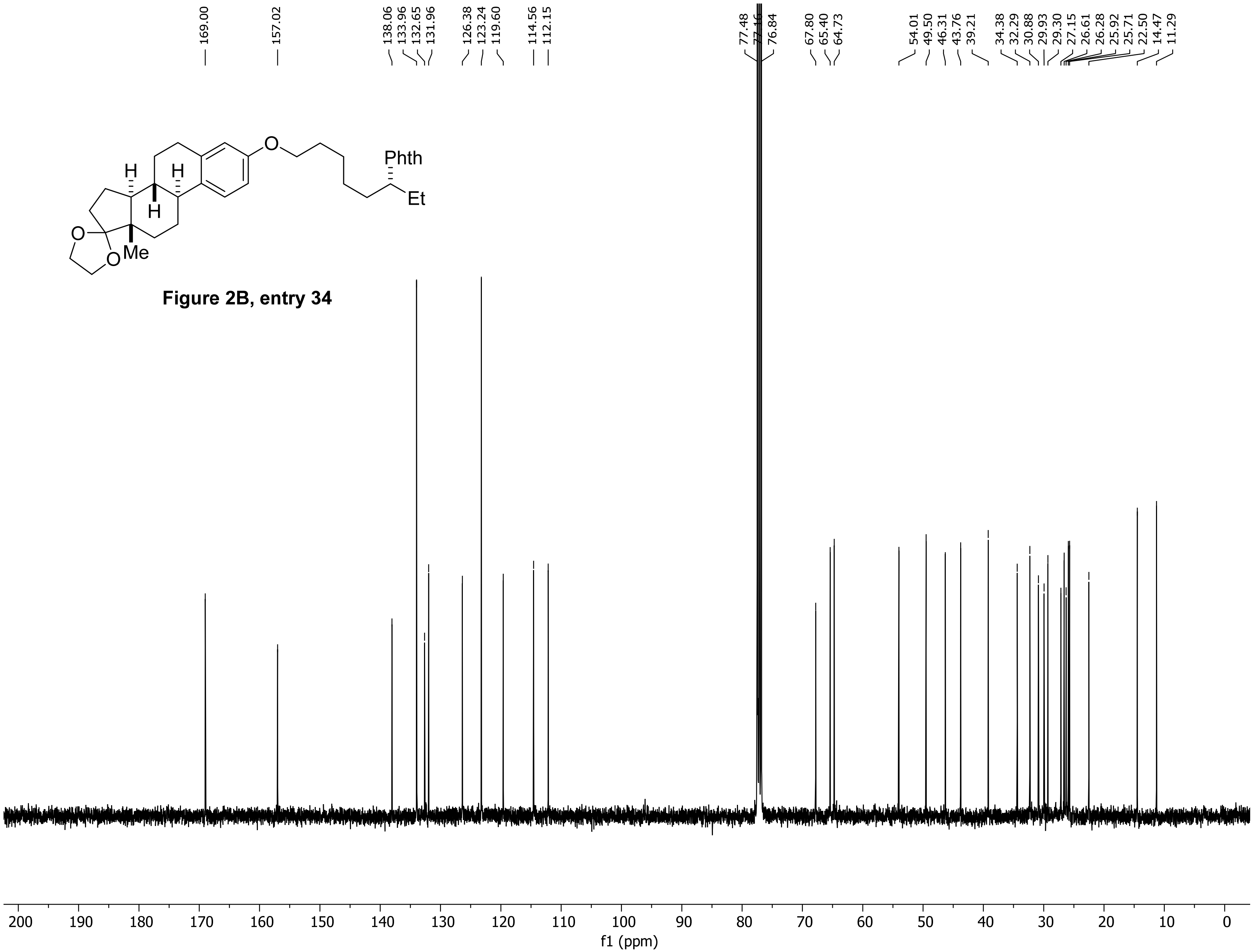


Figure 2B, entry 34

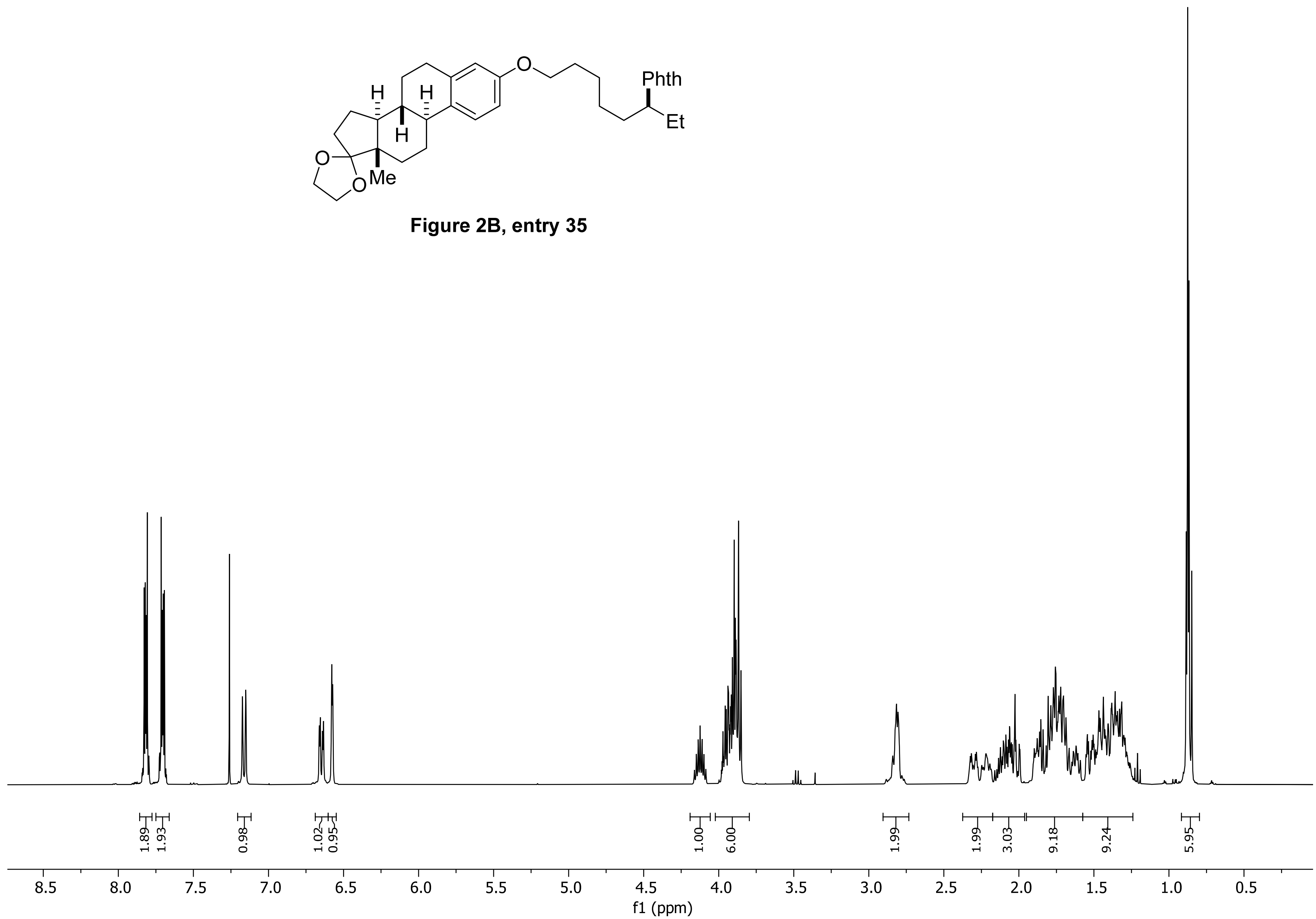


Figure 2B, entry 35

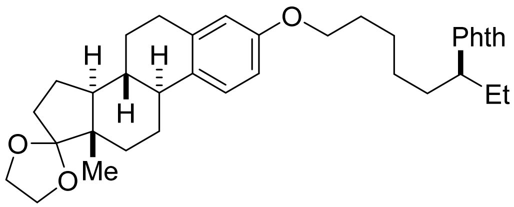
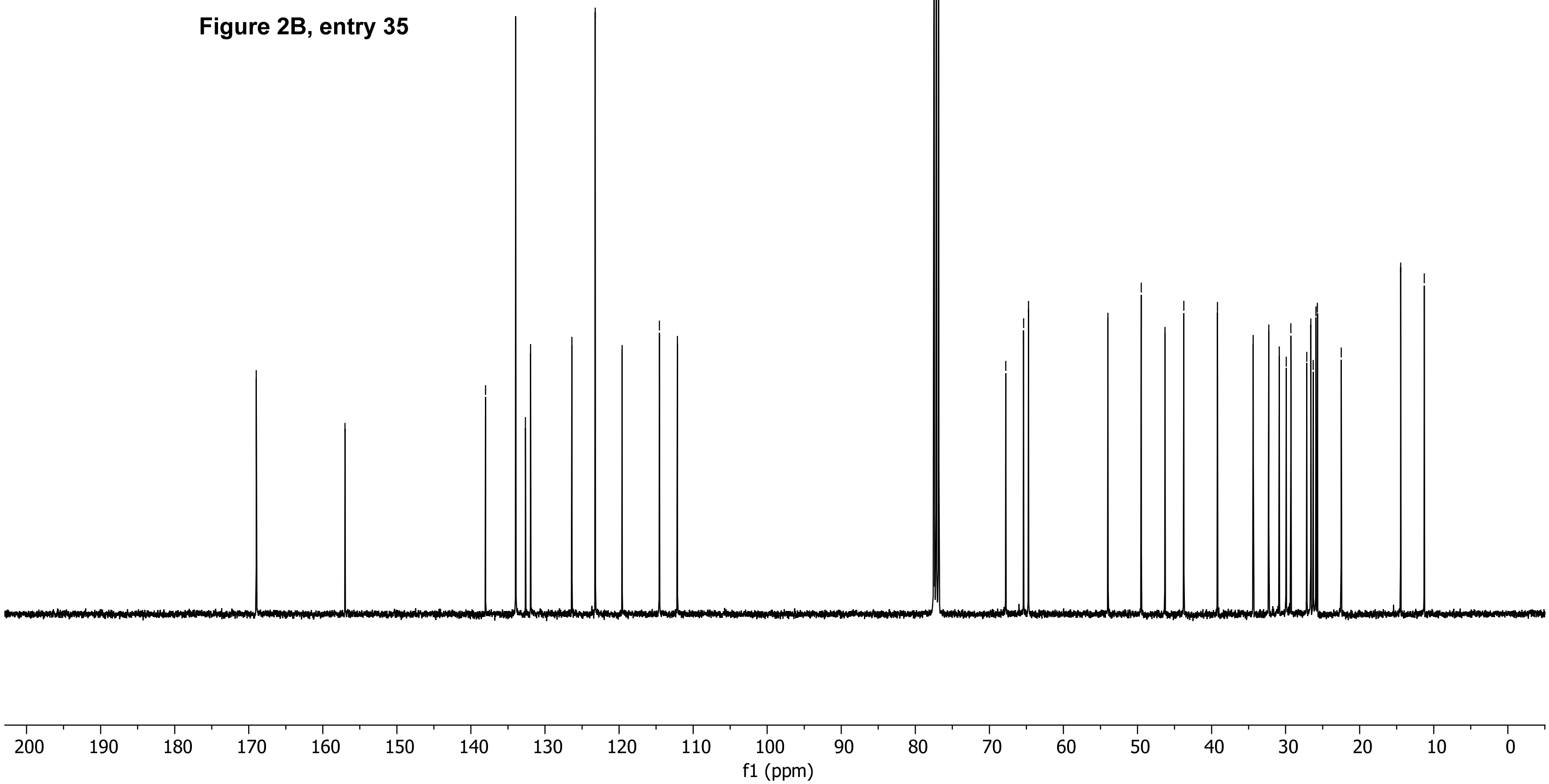
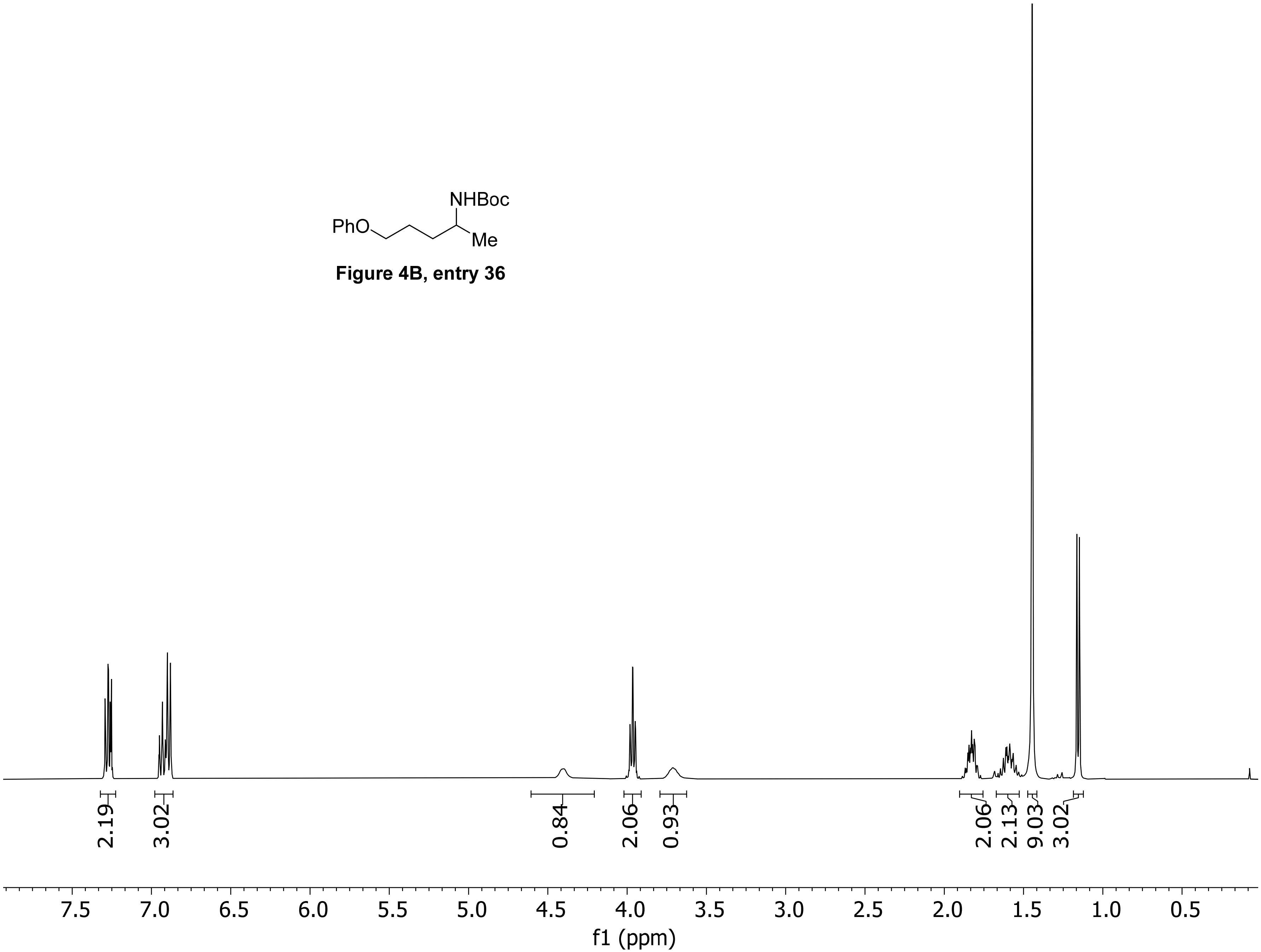


Figure 2B, entry 35




NHBoc
PhO
Me
Figure 4B, entry 36
2.19
3.02
0.84
2.06
0.93
2.06
2.13
9.03
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

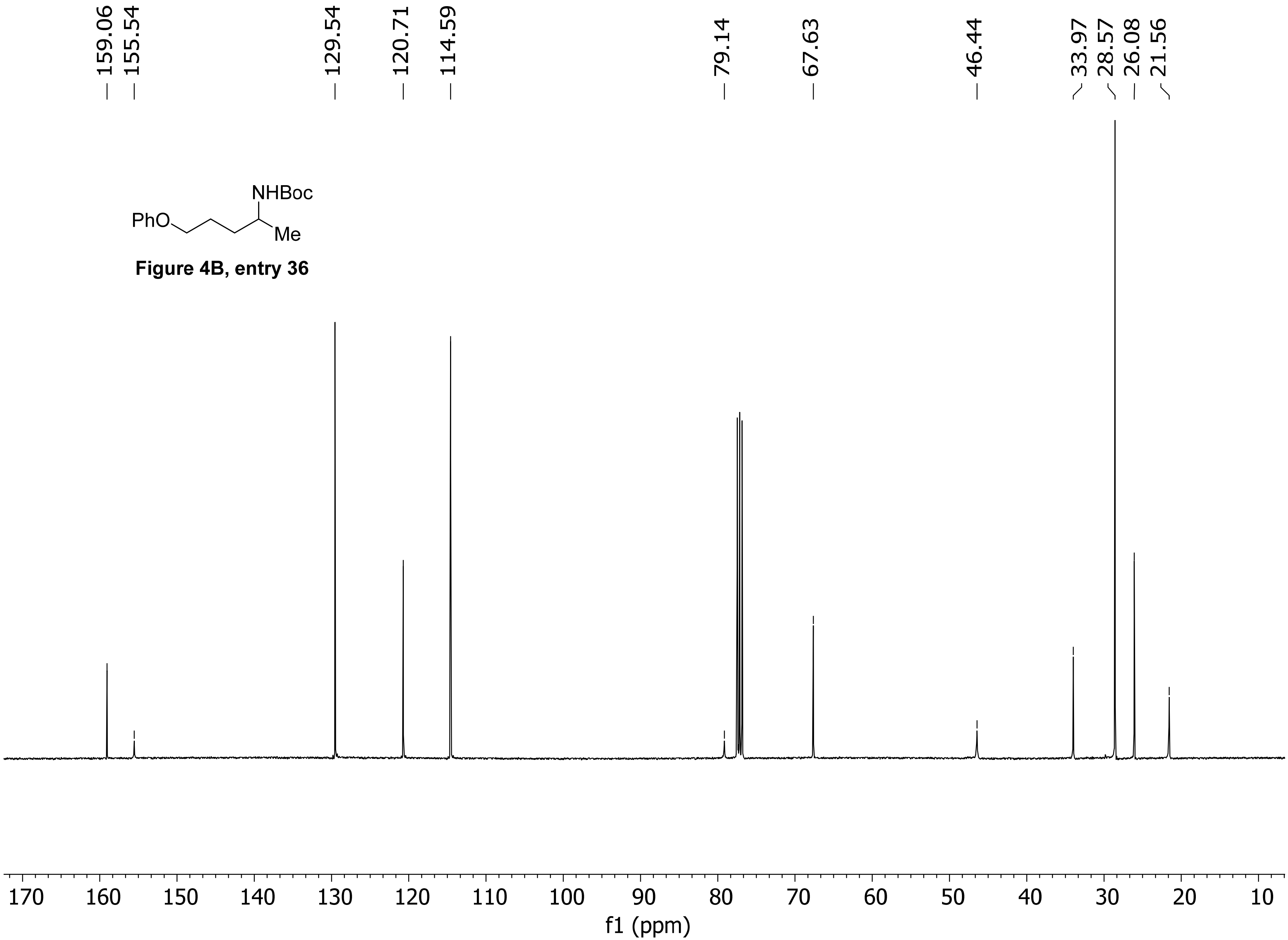


Figure 4B, entry 36

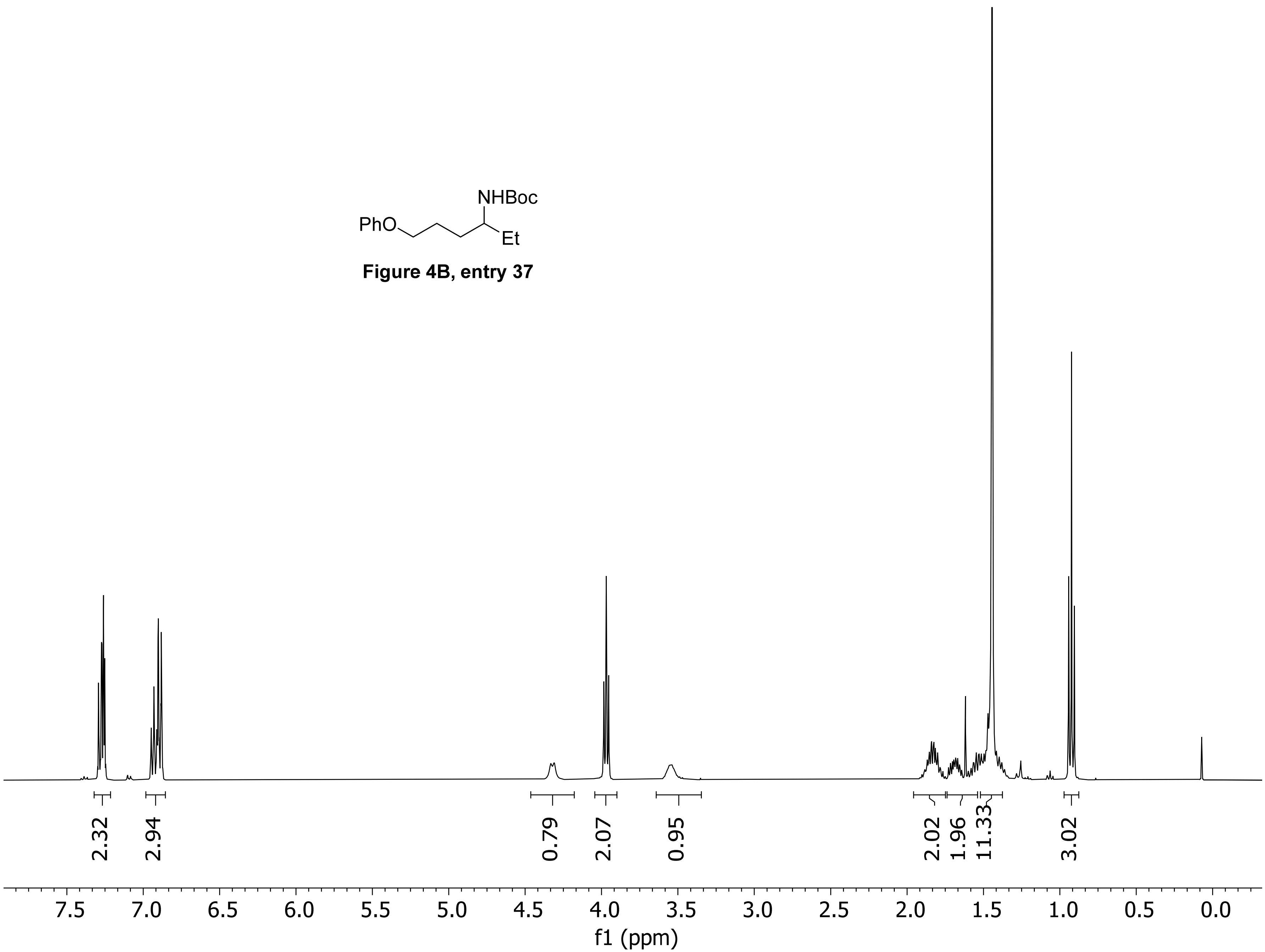
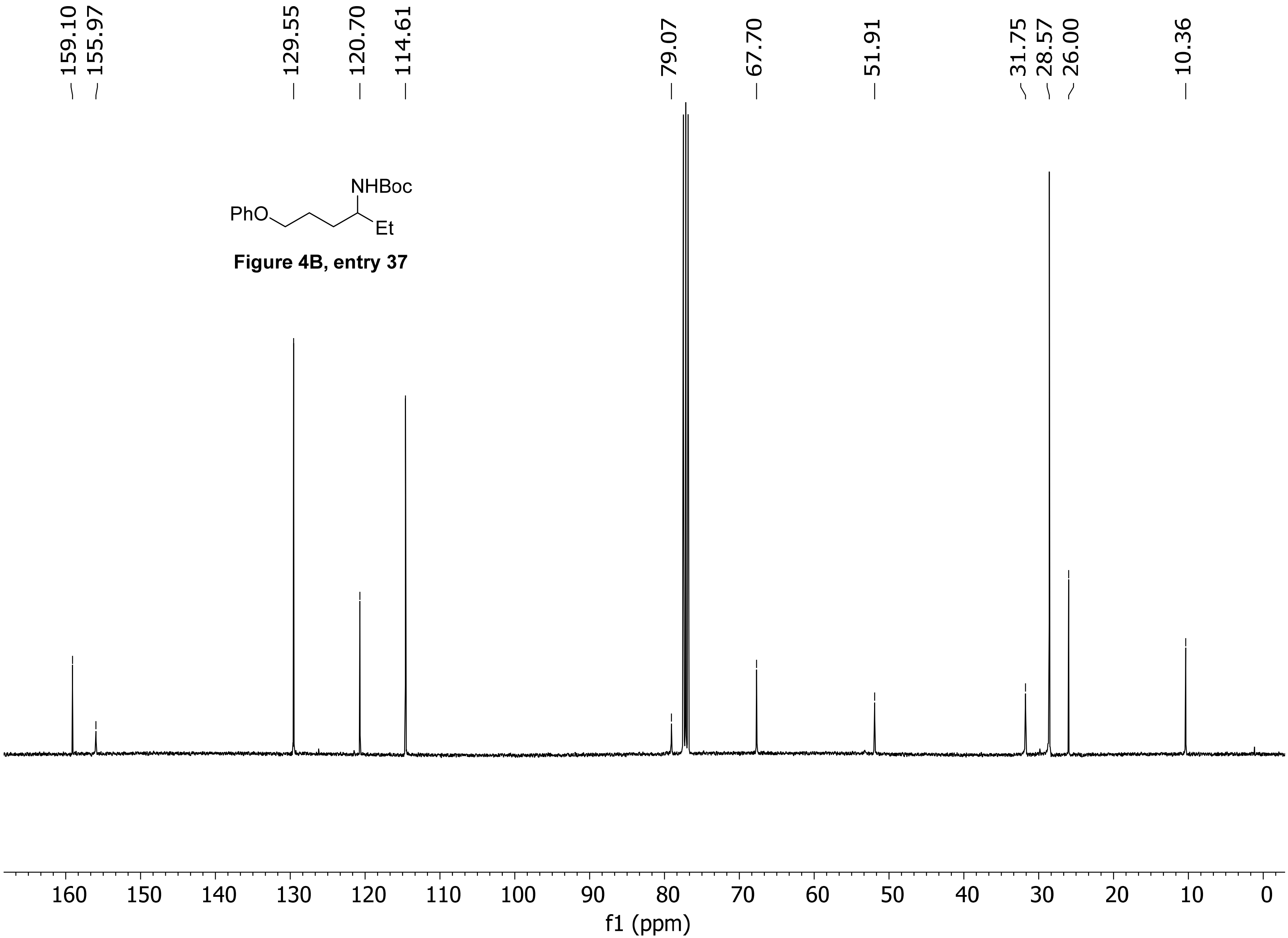


Figure 4B, entry 37


159.10
155.97
129.55
120.70
114.61
79.07
67.70
51.91
31.75
28.57
26.00
10.36
NHBoc
PhO
Et
Figure 4B, entry 37
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

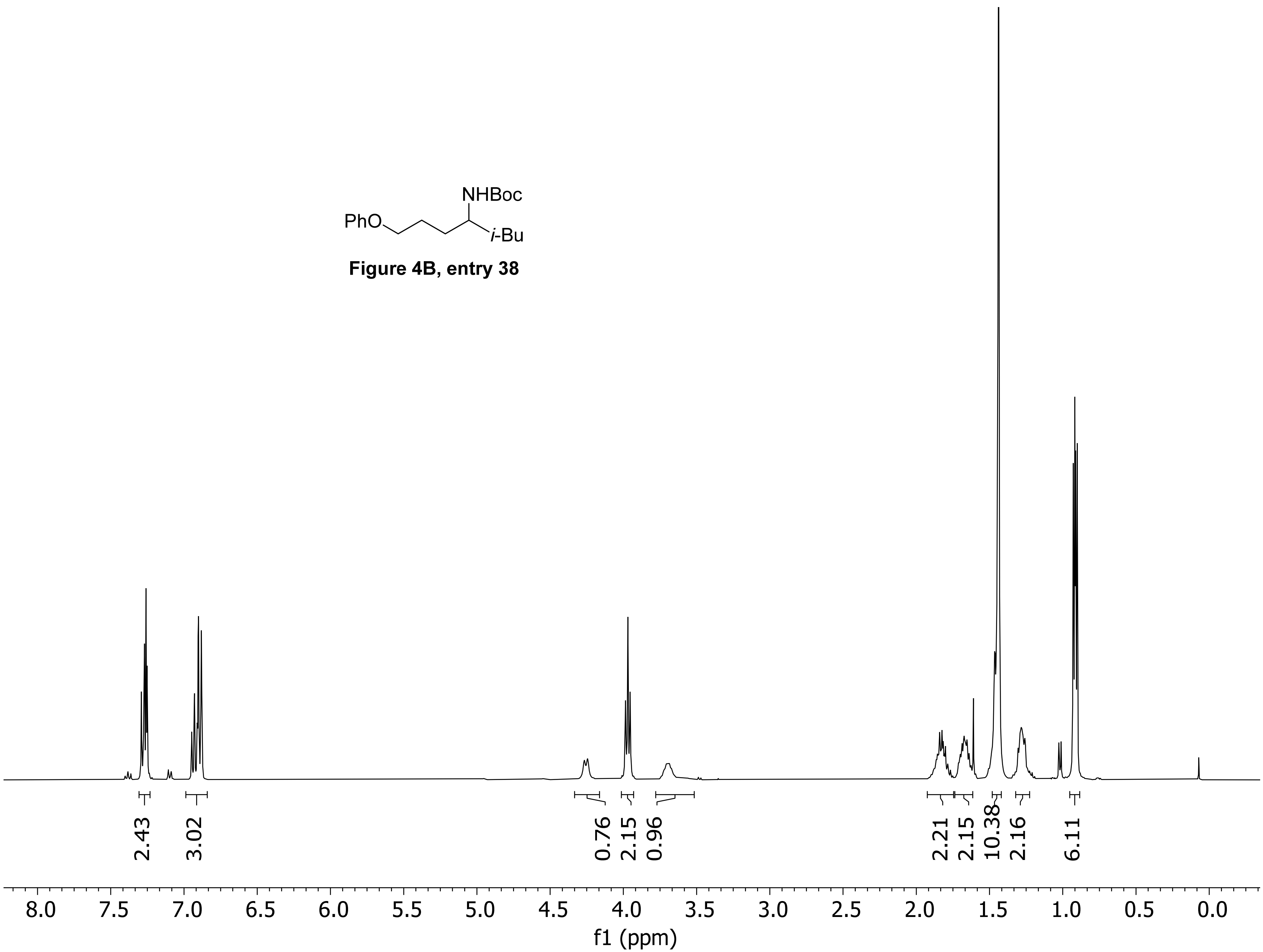
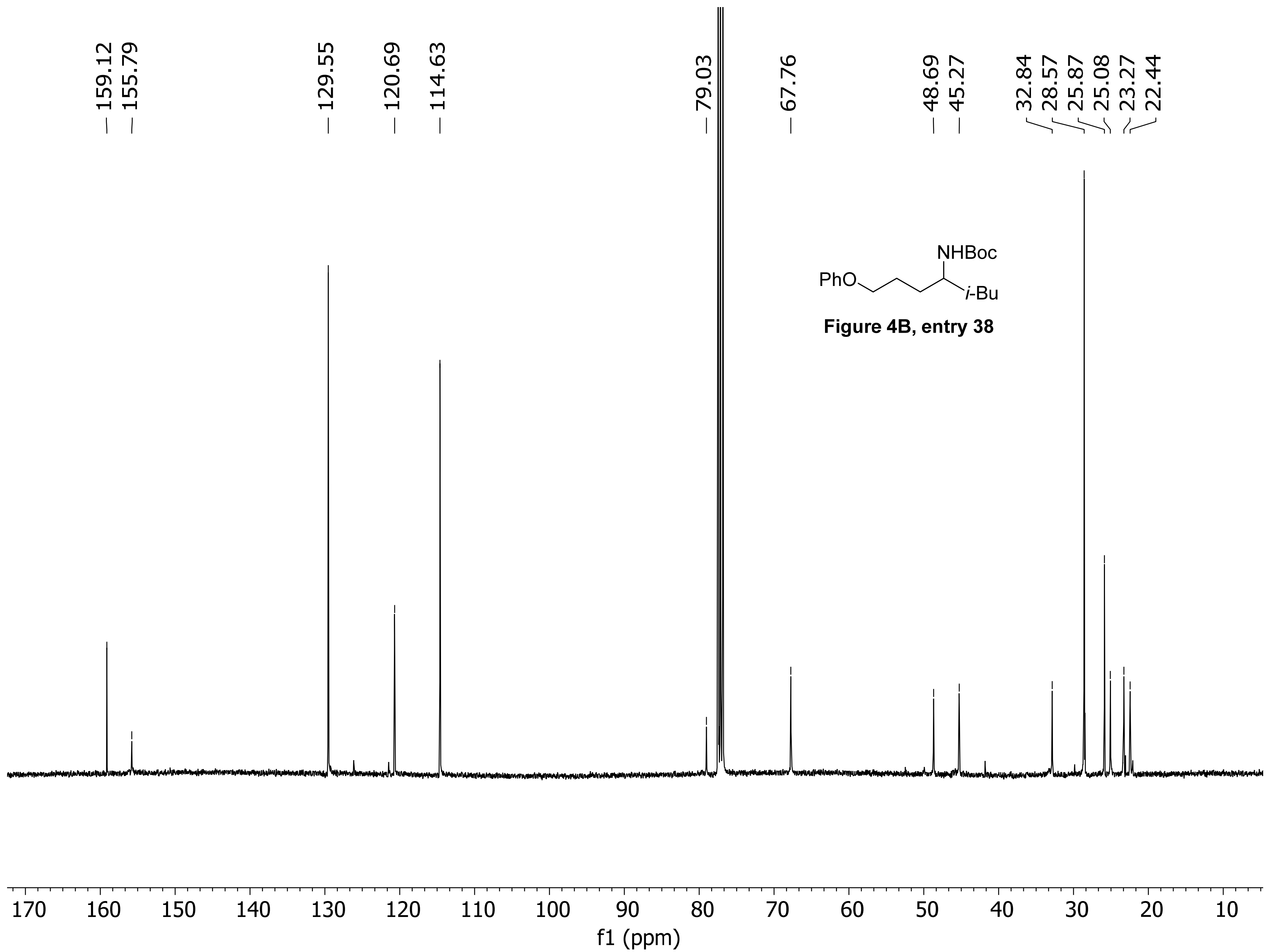


Figure 4B, entry 38


159.12
155.79
129.55
120.69
114.63
79.03
67.76
48.69
45.27
32.84
28.57
25.87
25.08
23.27
22.44
NHBoc
PhO
i-Bu
Figure 4B, entry 38
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

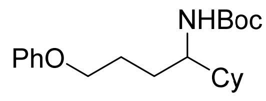
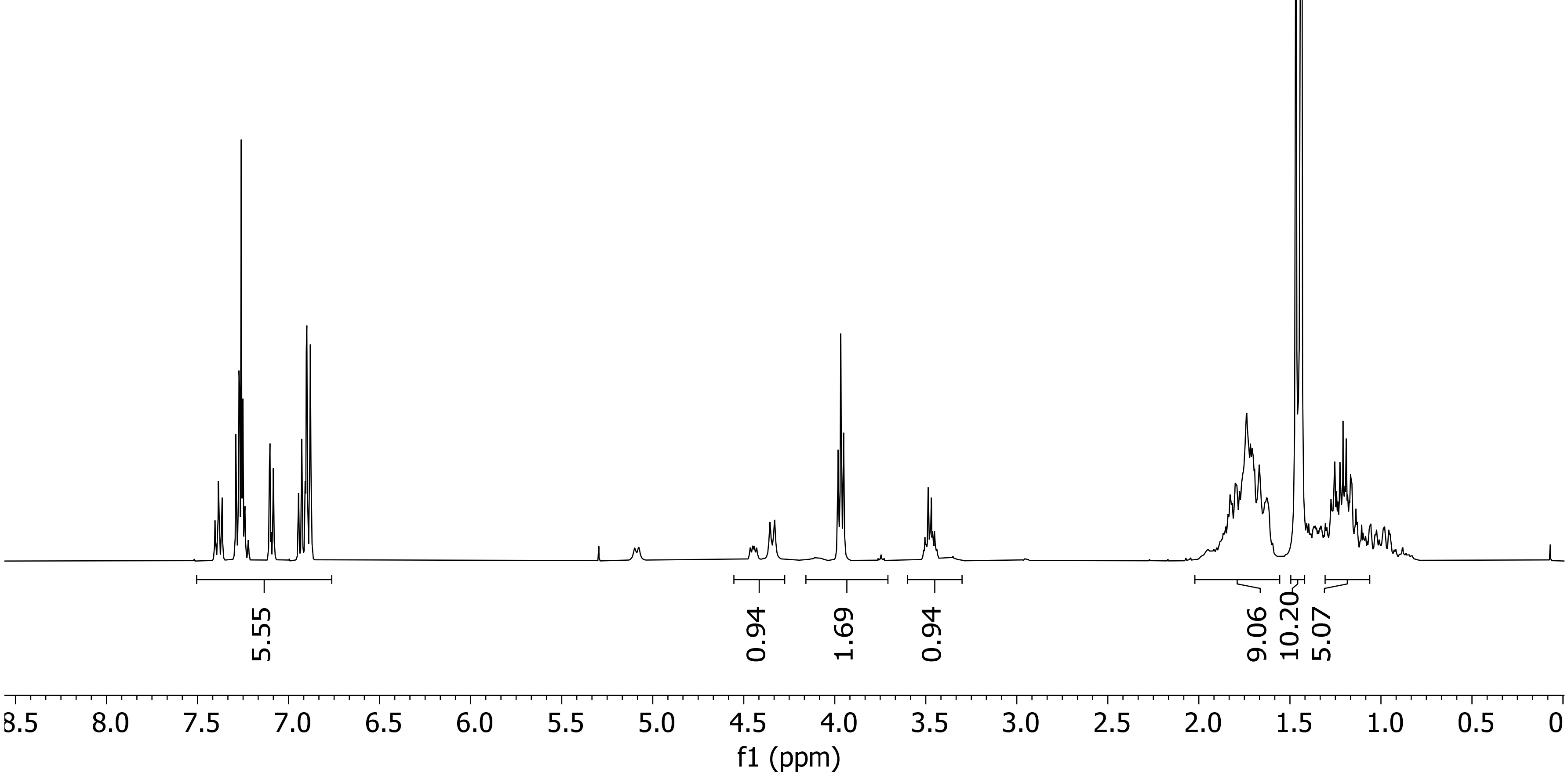


Figure 4B, entry 39



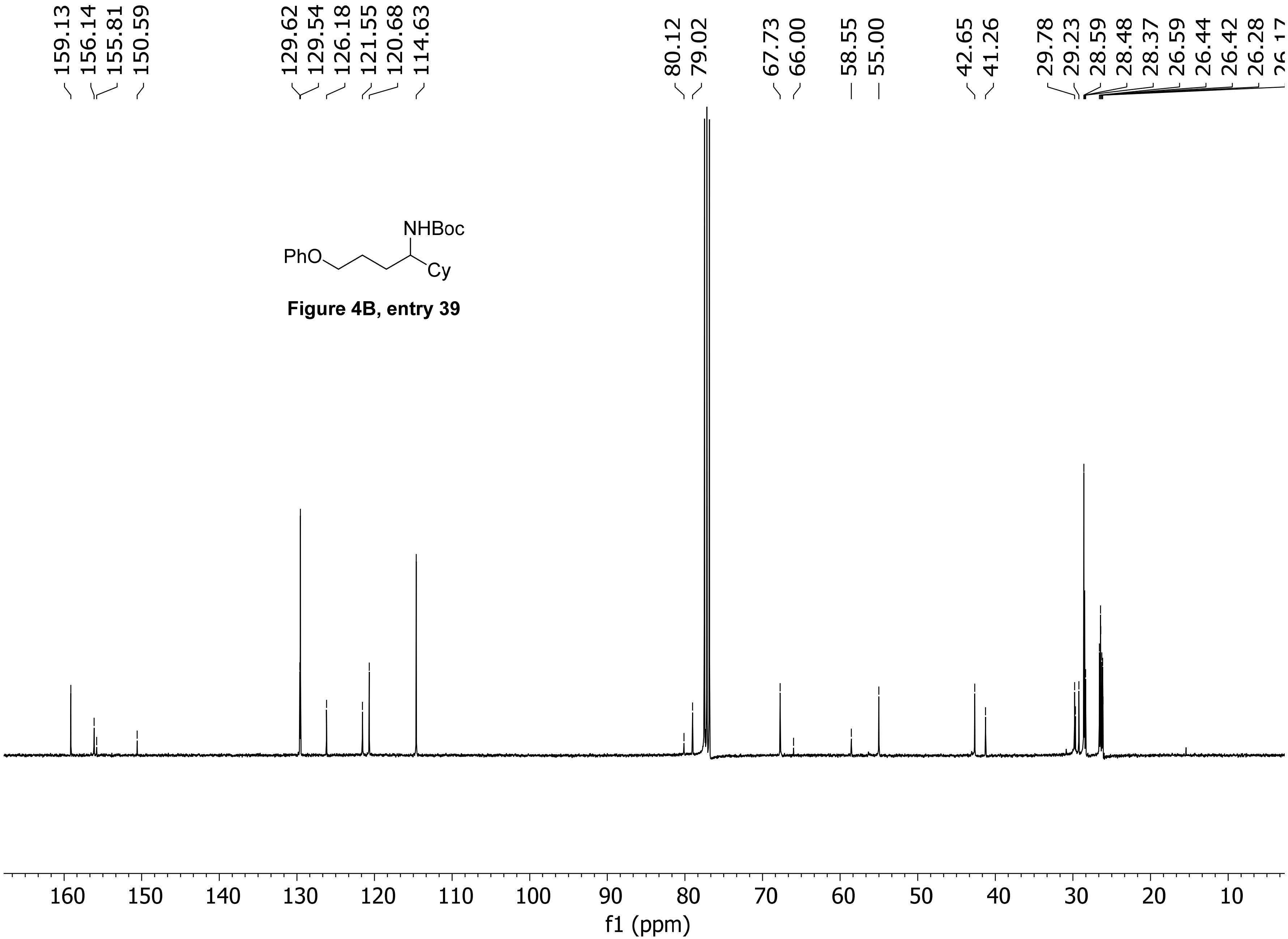


Figure 4B, entry 39

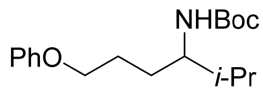
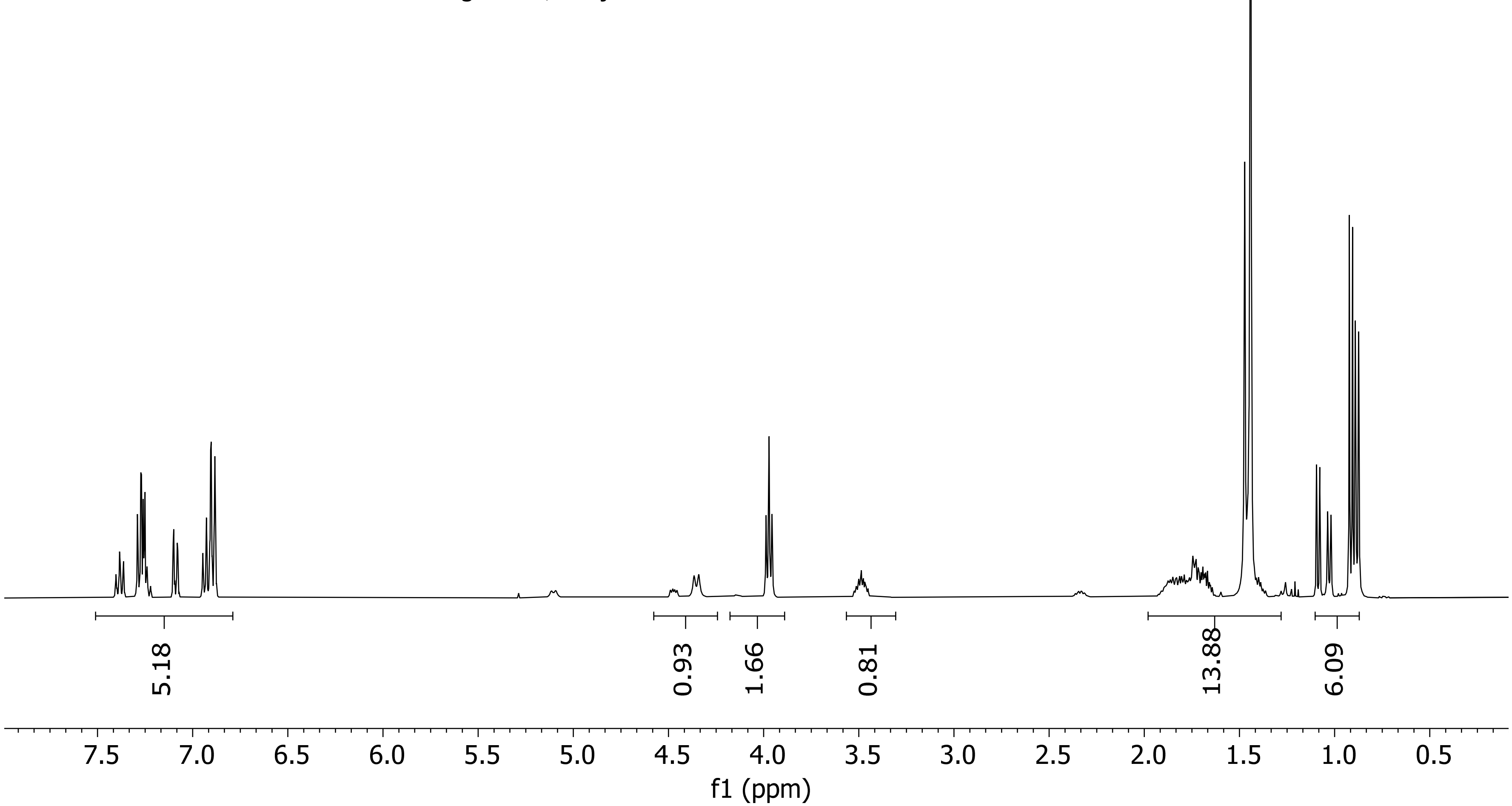
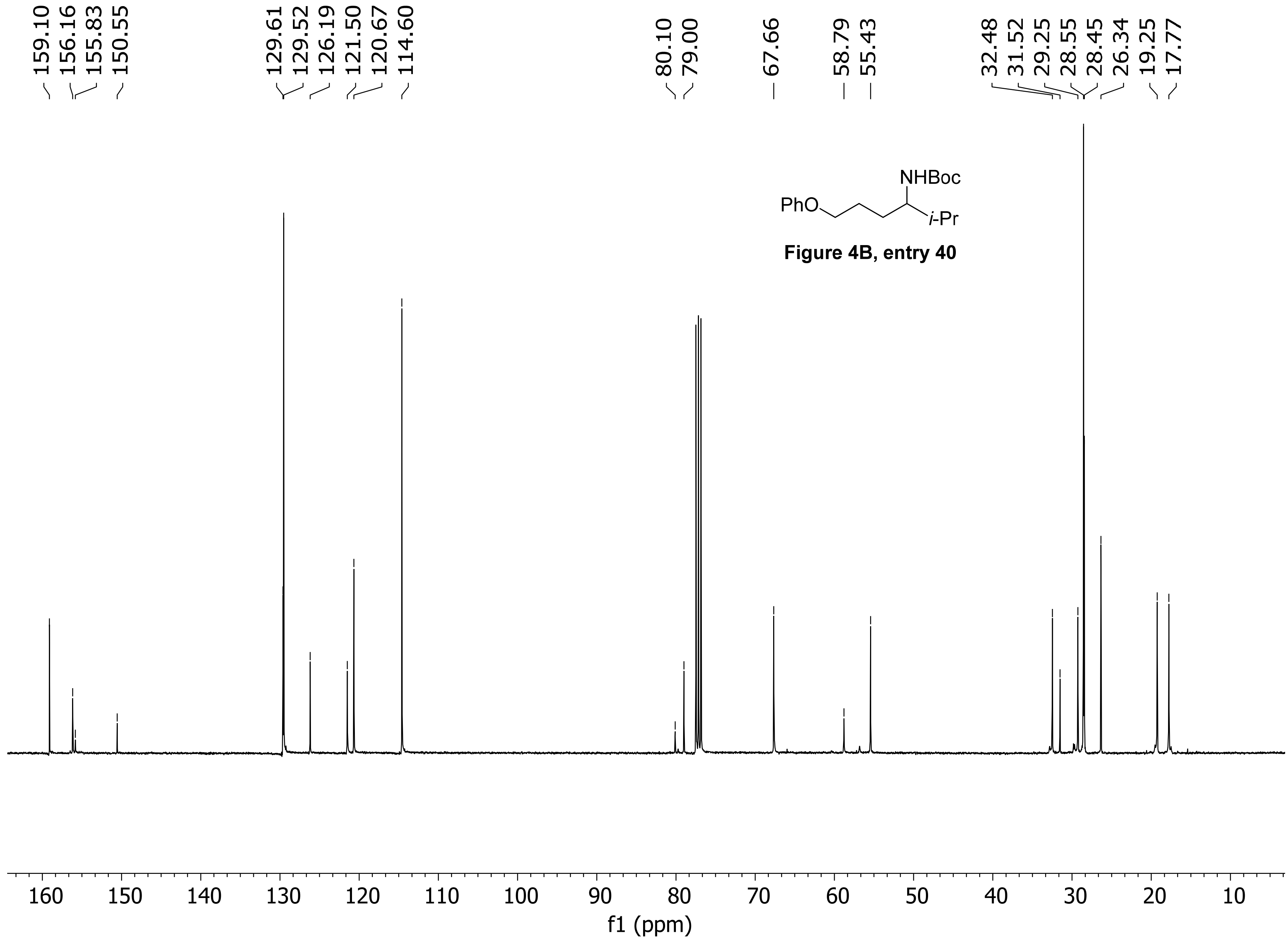
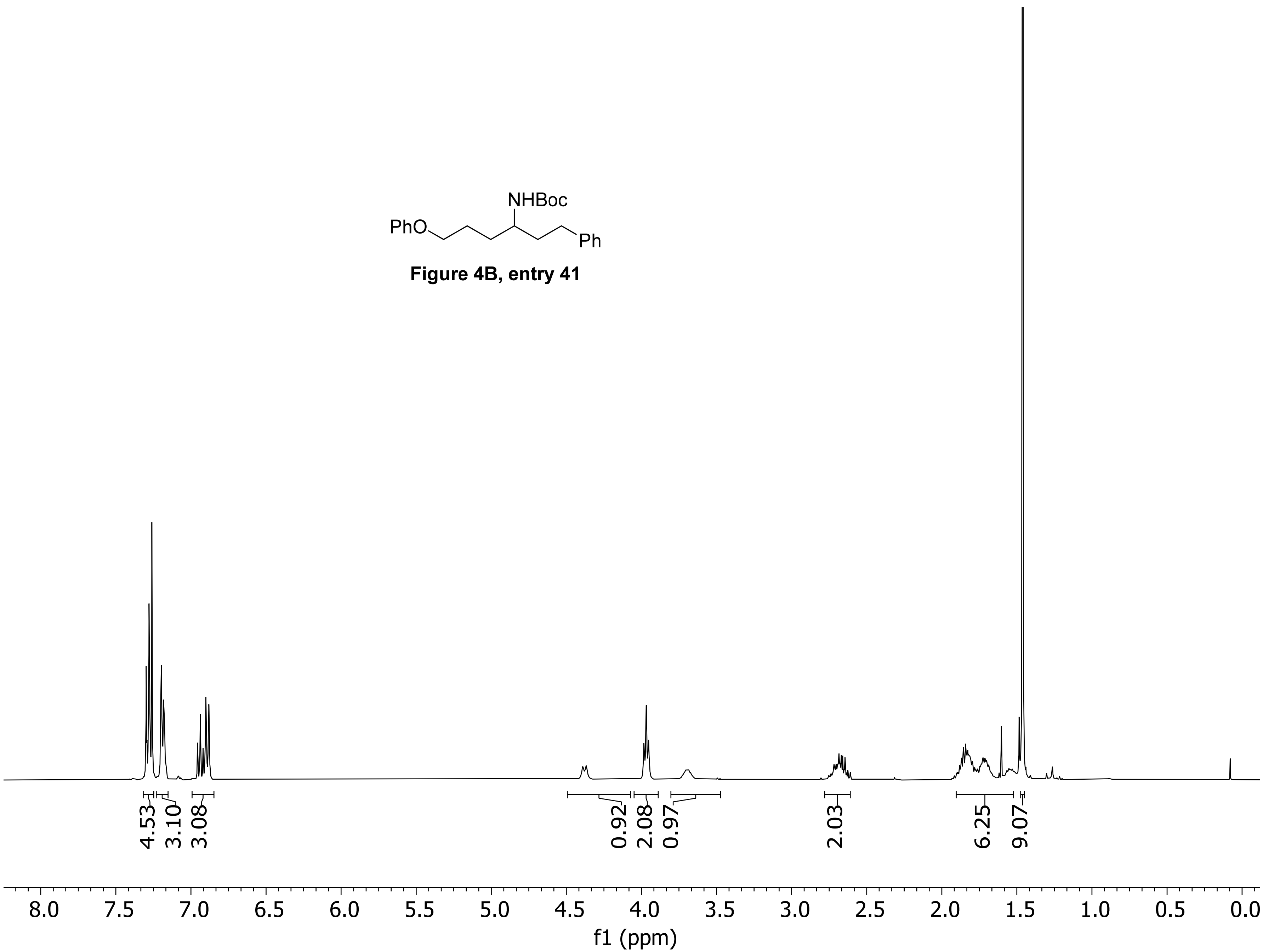


Figure 4B, entry 40




159.10
156.16
155.83
150.55
129.61
129.52
126.19
121.50
120.67
114.60
80.10
79.00
67.66
58.79
55.43
32.48
31.52
29.25
28.55
28.45
26.34
19.25
17.77
NHBoc
PhO
i-Pr
Figure 4B, entry 40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


NHBoc
PhO
Ph
Figure 4B, entry 41
4.53
3.10
3.08
0.92
2.08
0.97
2.03
6.25
9.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

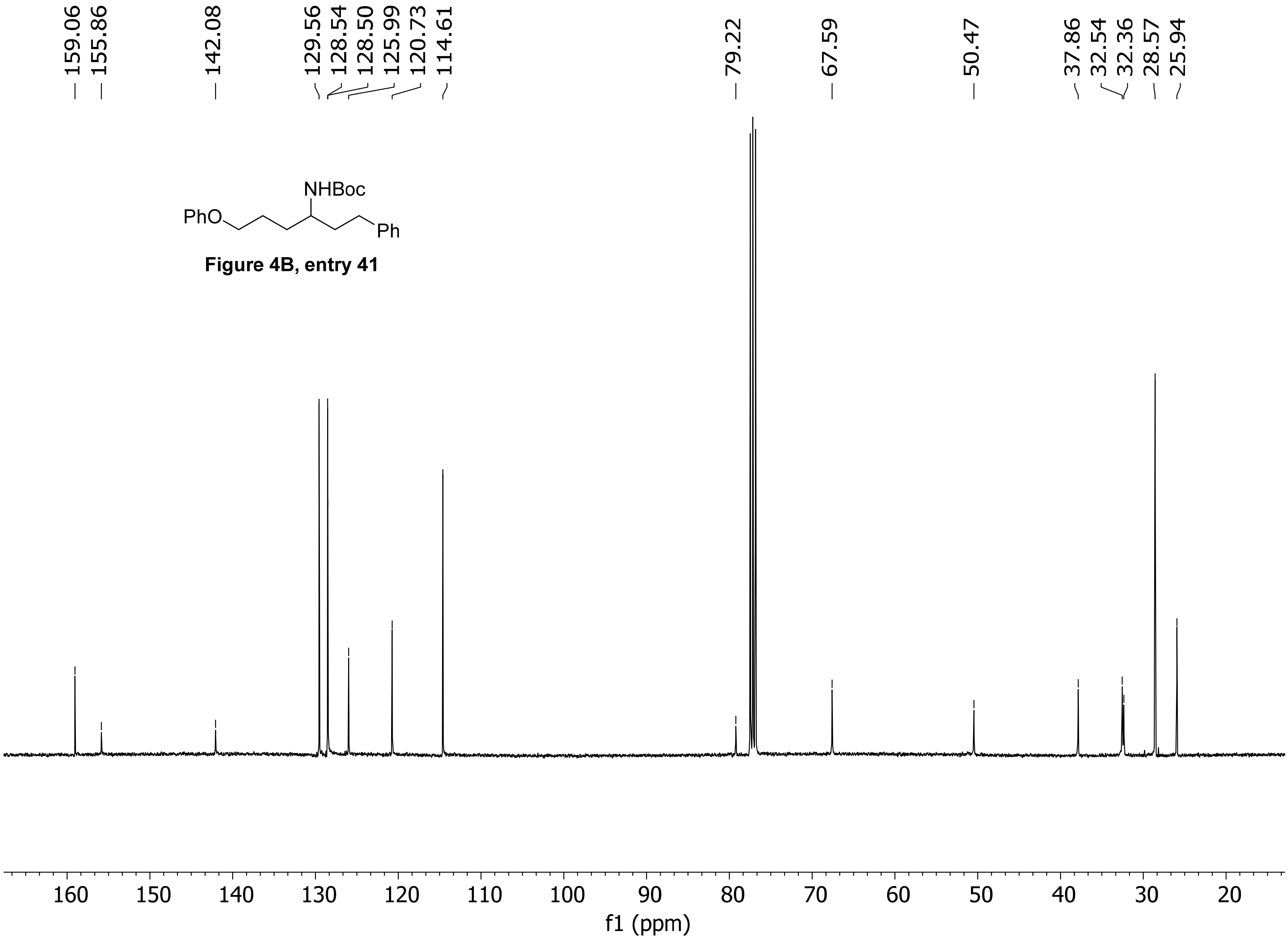
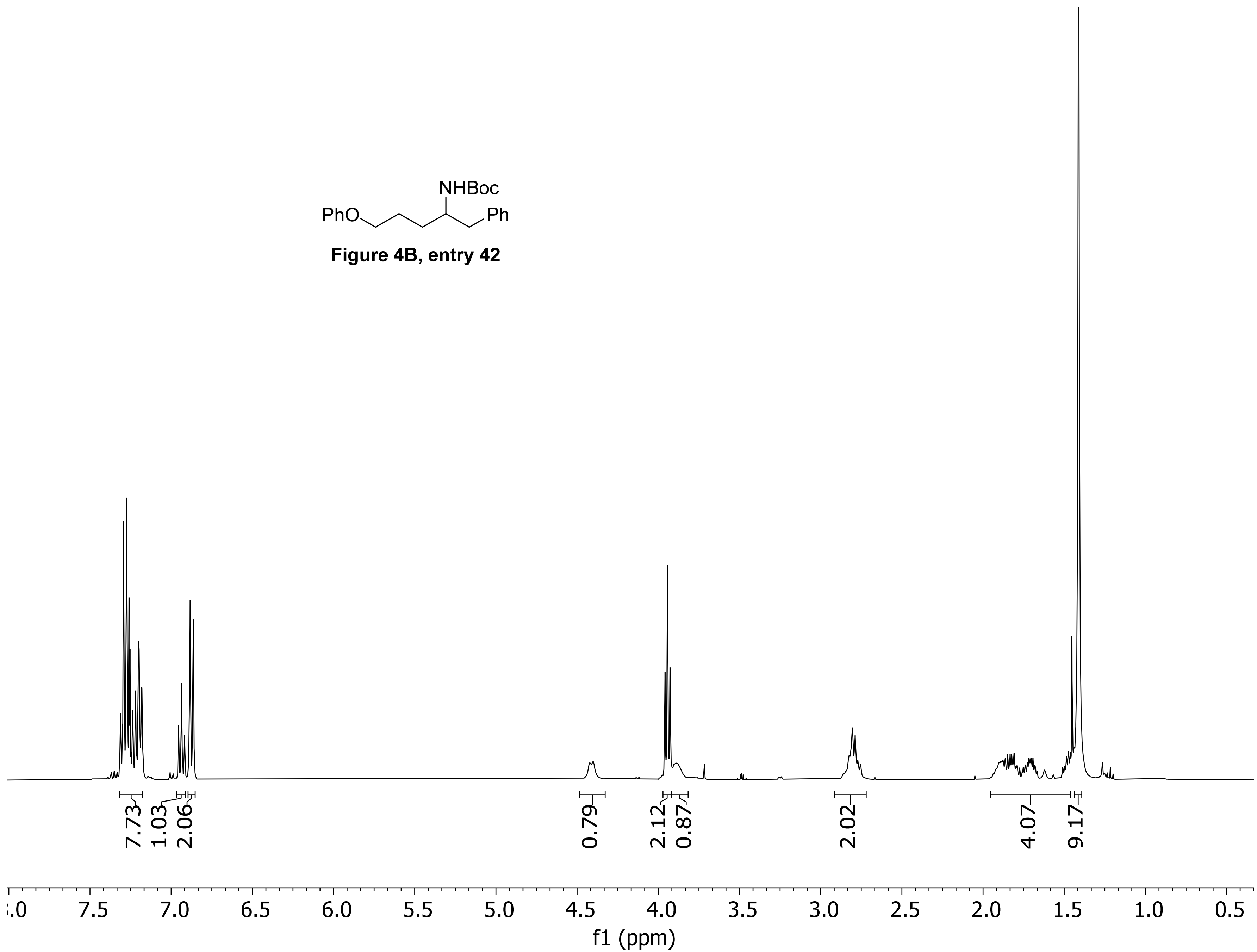
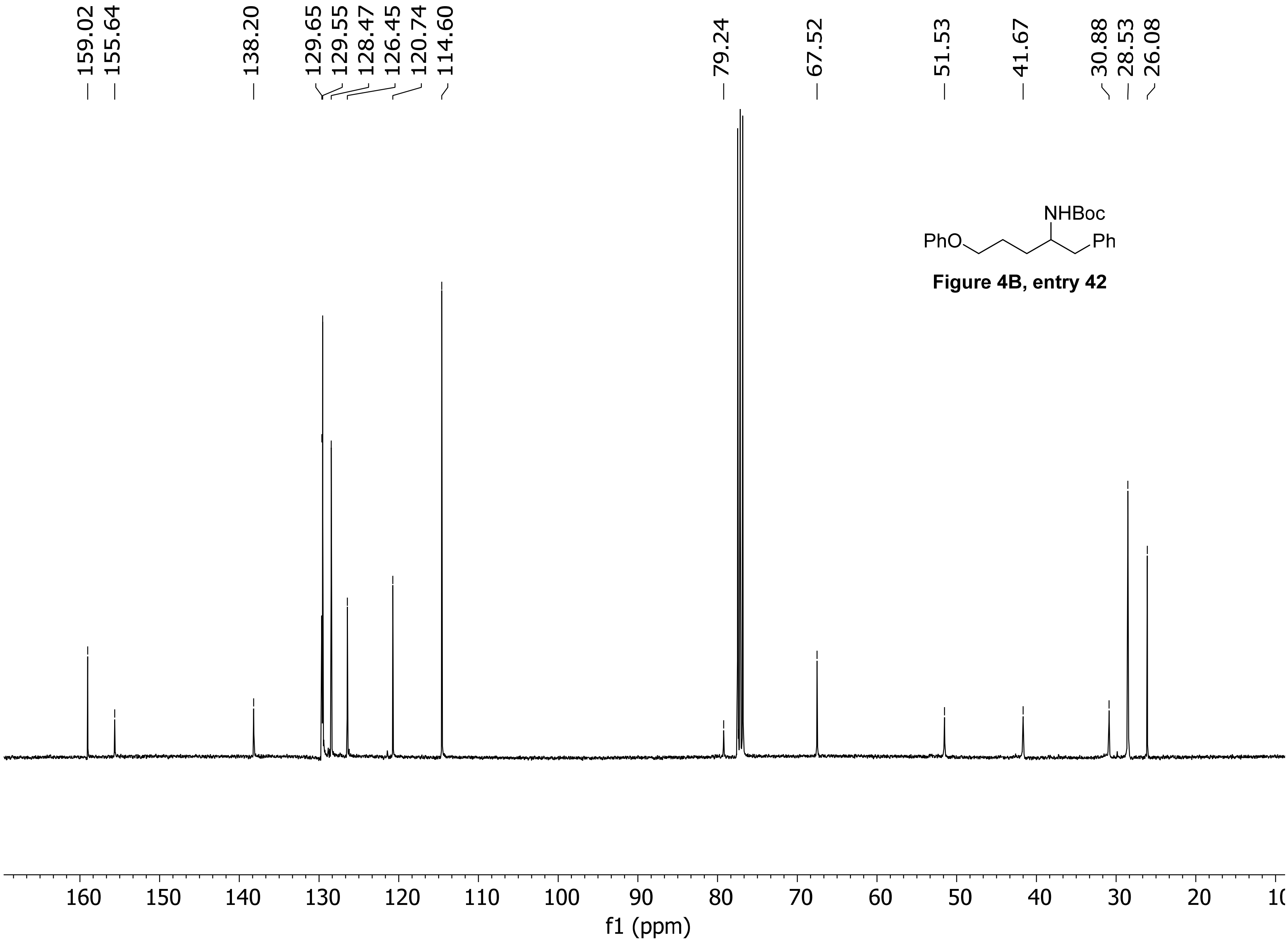


Figure 4B, entry 41


NHBoc
PhO
Ph
Figure 4B, entry 42
7.73
1.03
2.06
0.79
2.12
0.87
2.02
4.07
9.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


159.02
155.64
138.20
129.65
129.55
128.47
126.45
120.74
114.60
79.24
67.52
51.53
41.67
30.88
28.53
26.08
NHBoc
PhO
Ph
Figure 4B, entry 42
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

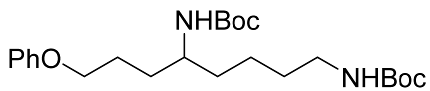
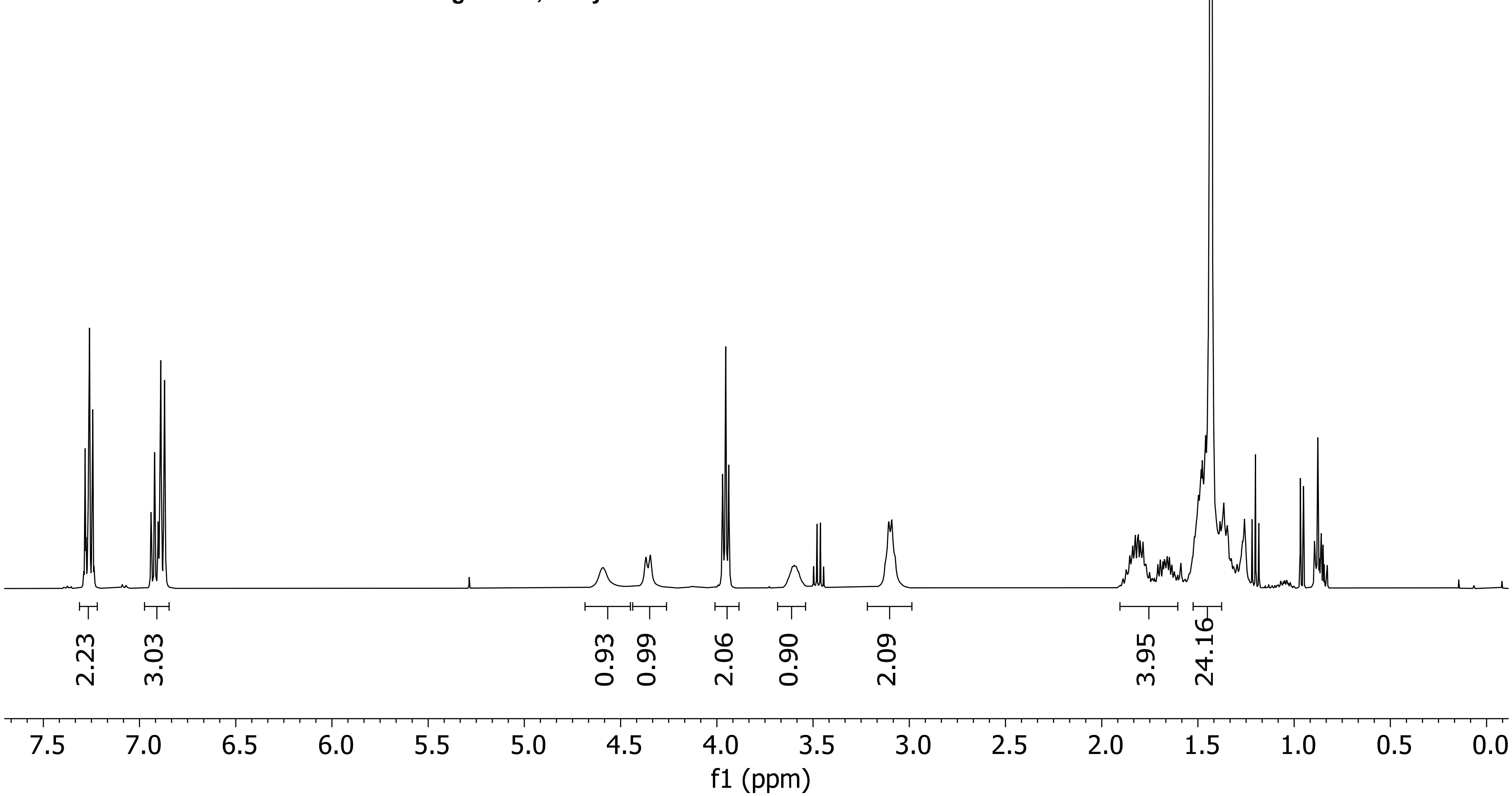


Figure 4B, entry 43



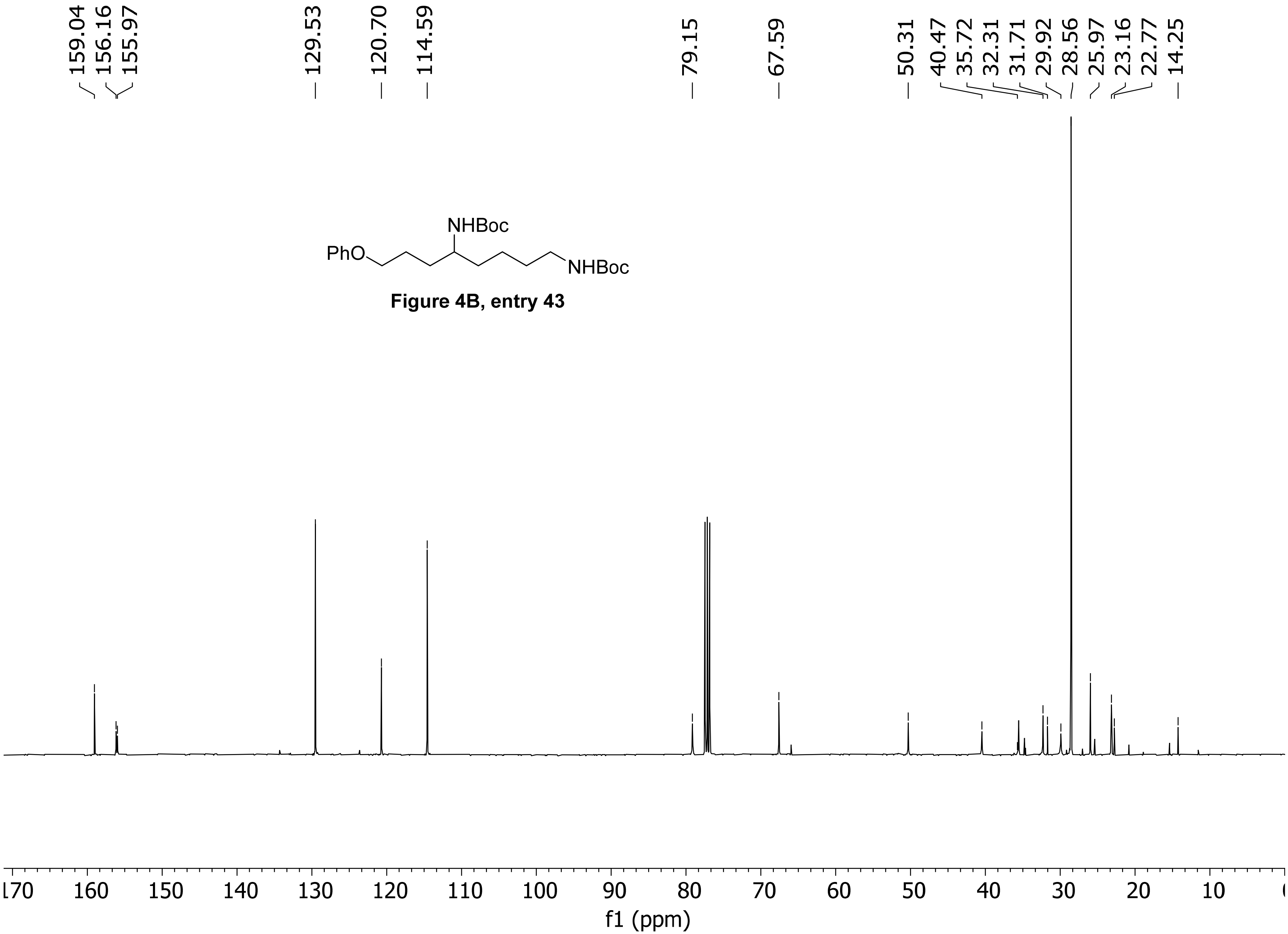


Figure 4B, entry 43

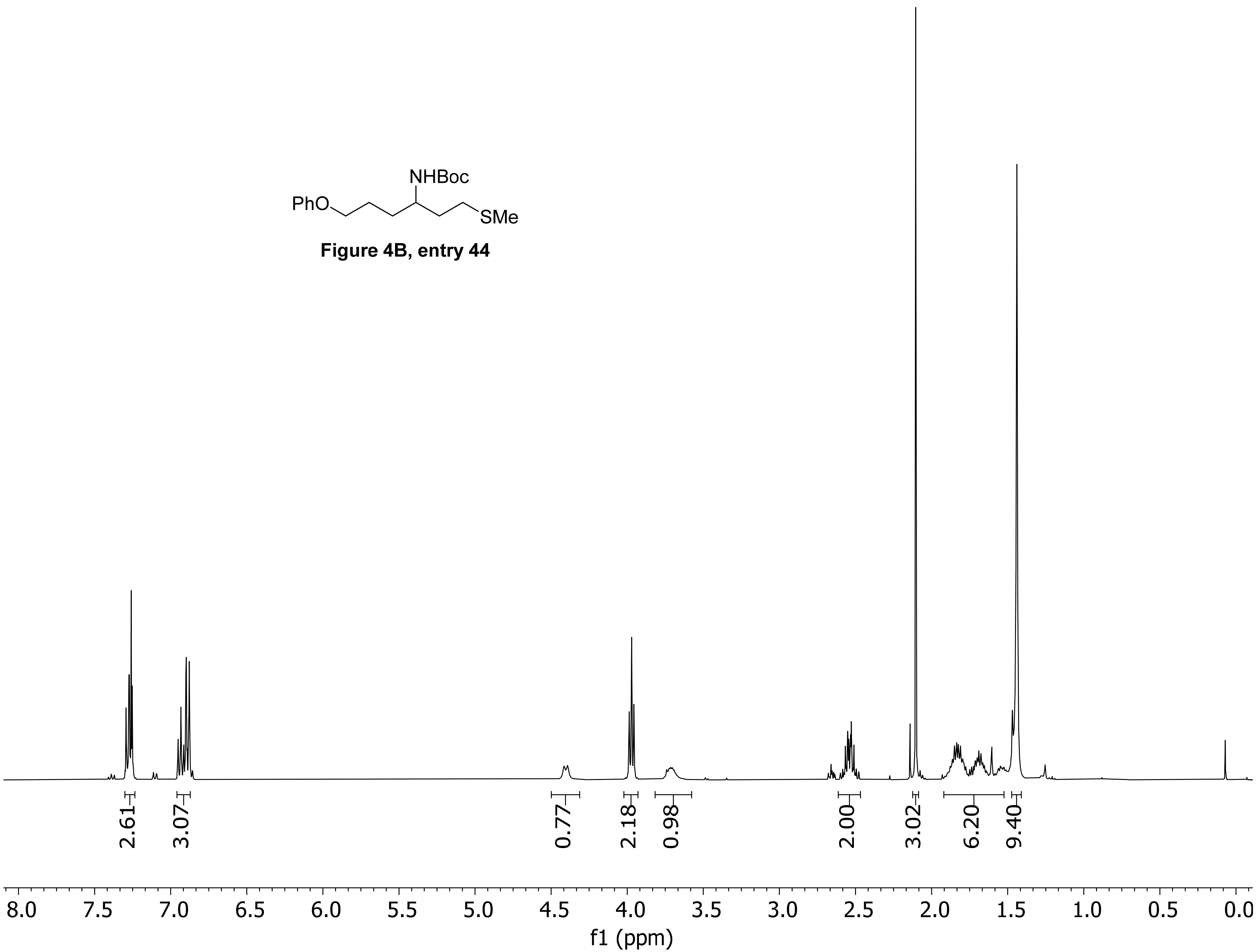
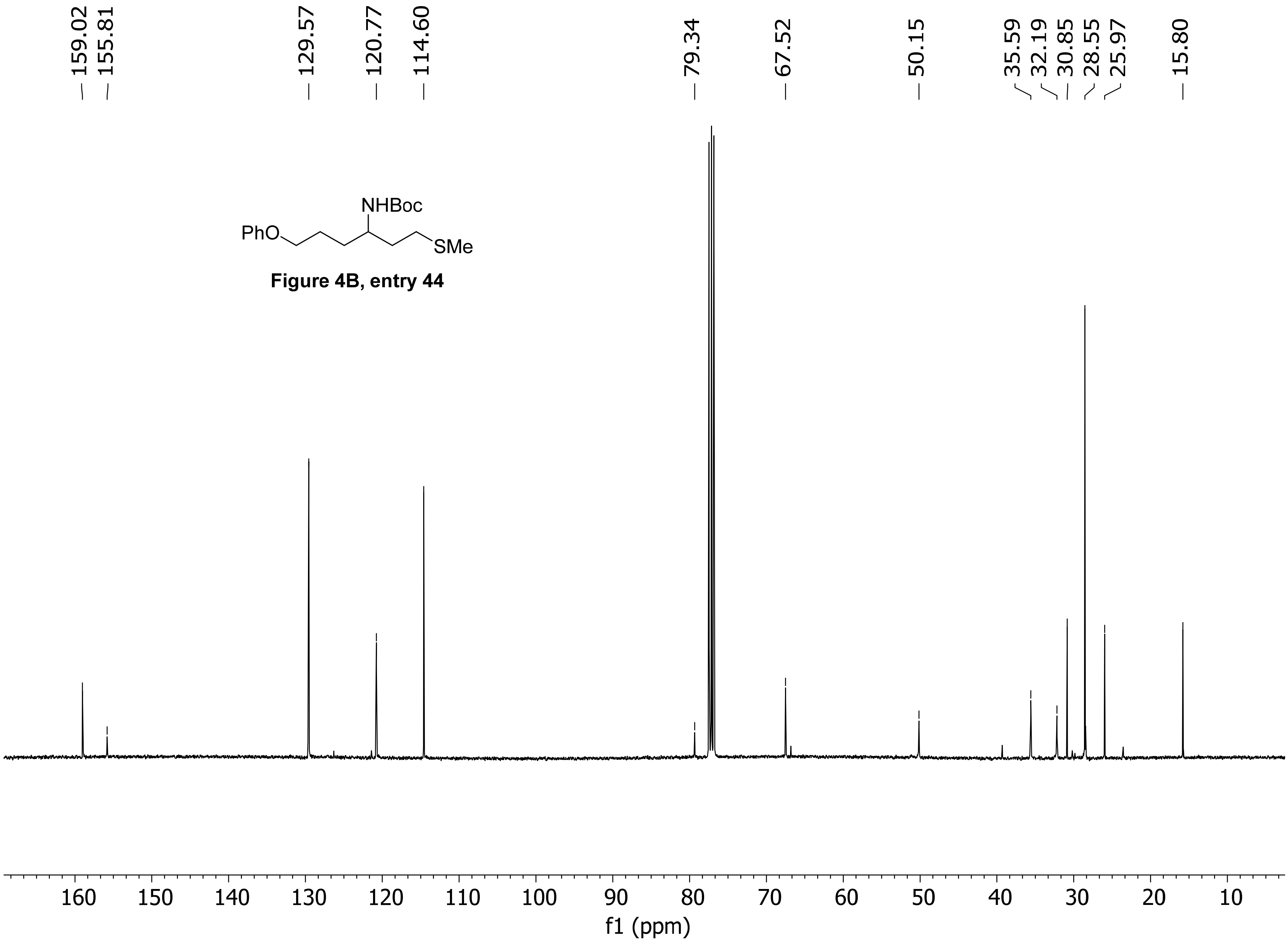


Figure 4B, entry 44


159.02
155.81
129.57
120.77
114.60
79.34
67.52
50.15
35.59
32.19
30.85
28.55
25.97
15.80
NHBoc
PhO
SMe
Figure 4B, entry 44
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

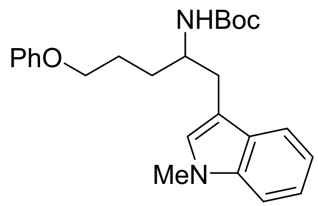
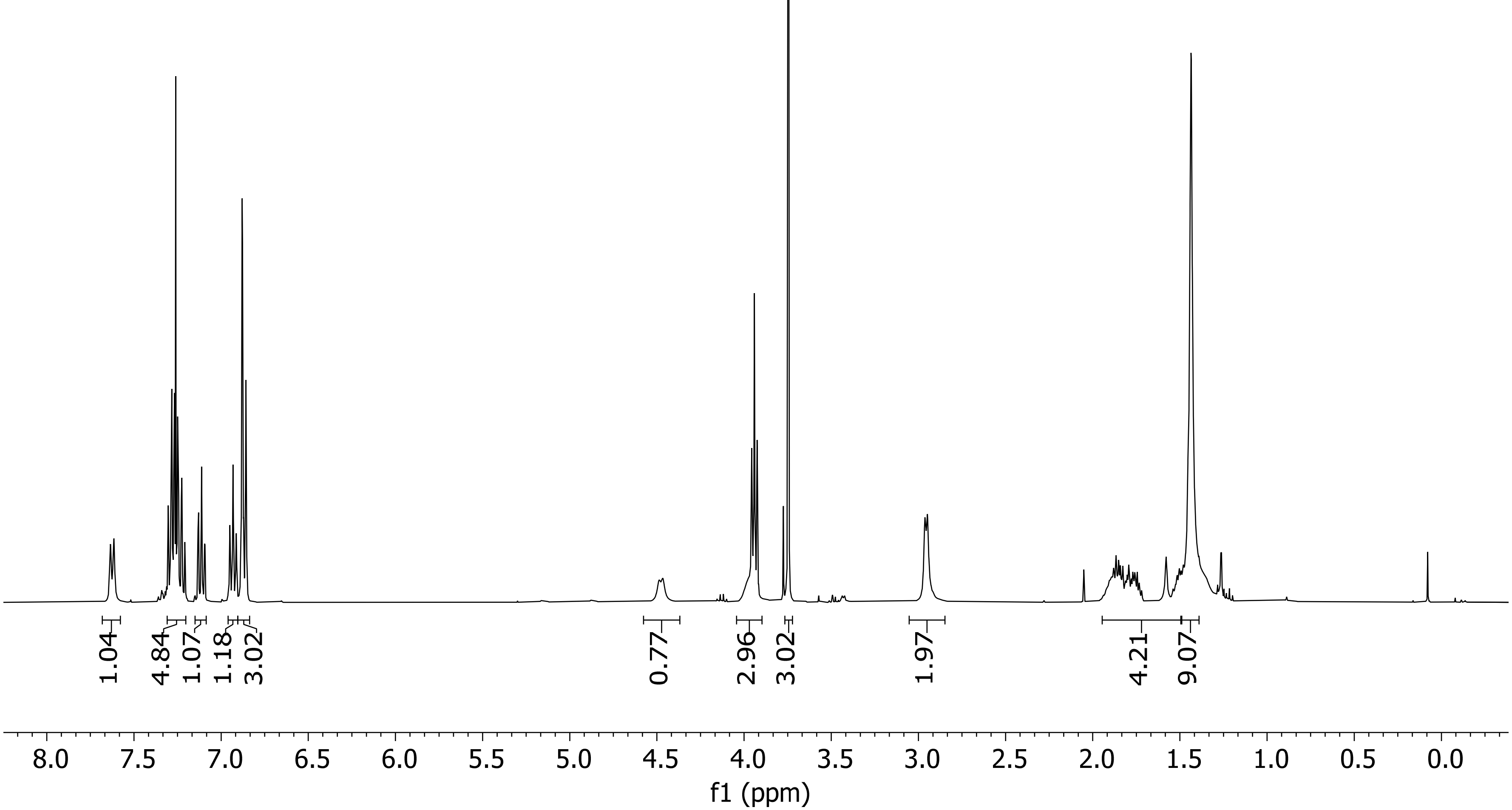
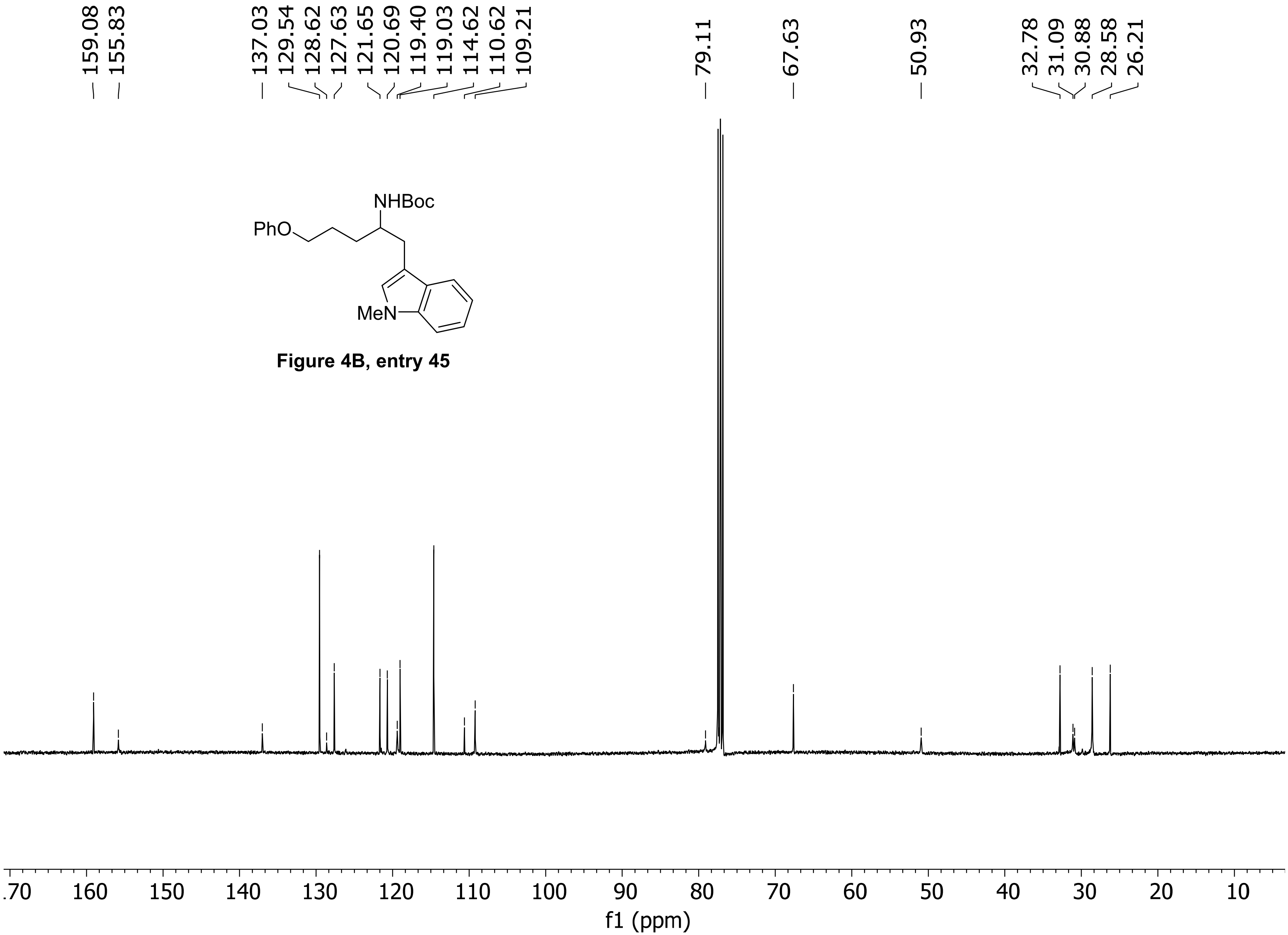
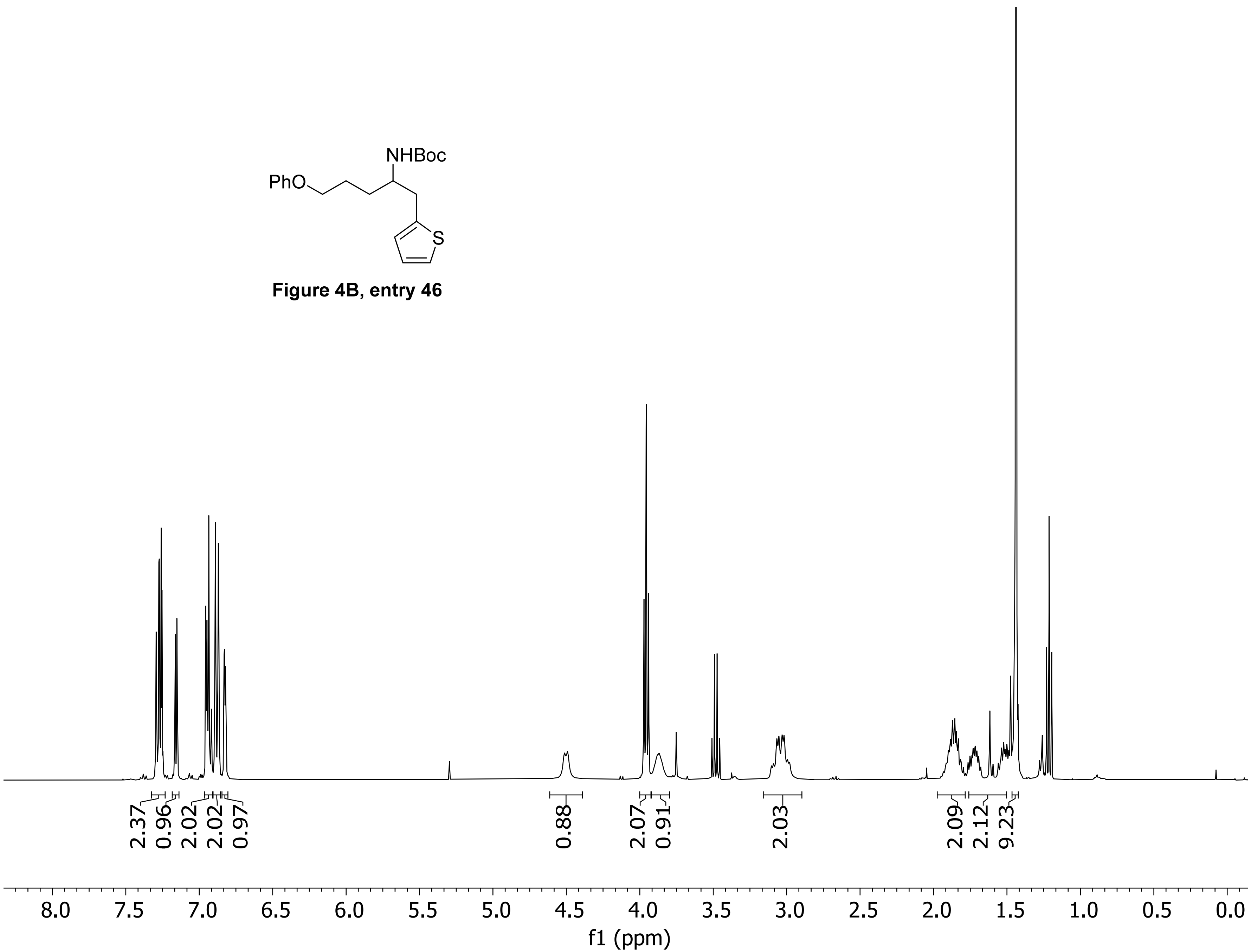


Figure 4B, entry 45




159.08
155.83
137.03
129.54
128.62
127.63
121.65
120.69
119.40
119.03
114.62
110.62
109.21
79.11
67.63
50.93
32.78
31.09
30.88
28.58
26.21
NHBoc
PhO
MeN
Figure 4B, entry 45
.70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


NHBoc
PhO
S
Figure 4B, entry 46
2.37
0.96
2.02
2.02
0.97
0.88
2.07
0.91
2.03
2.09
2.12
9.23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

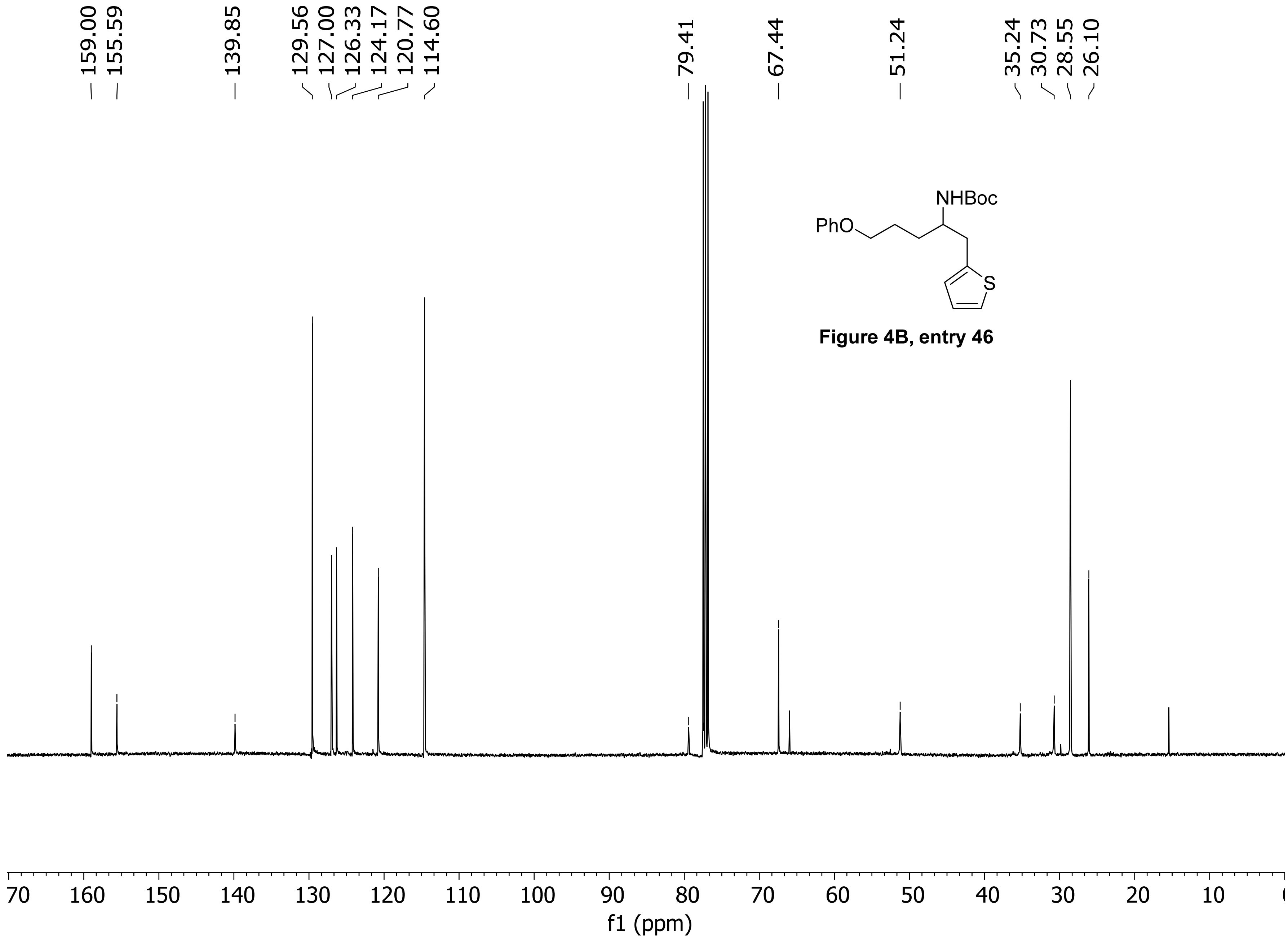
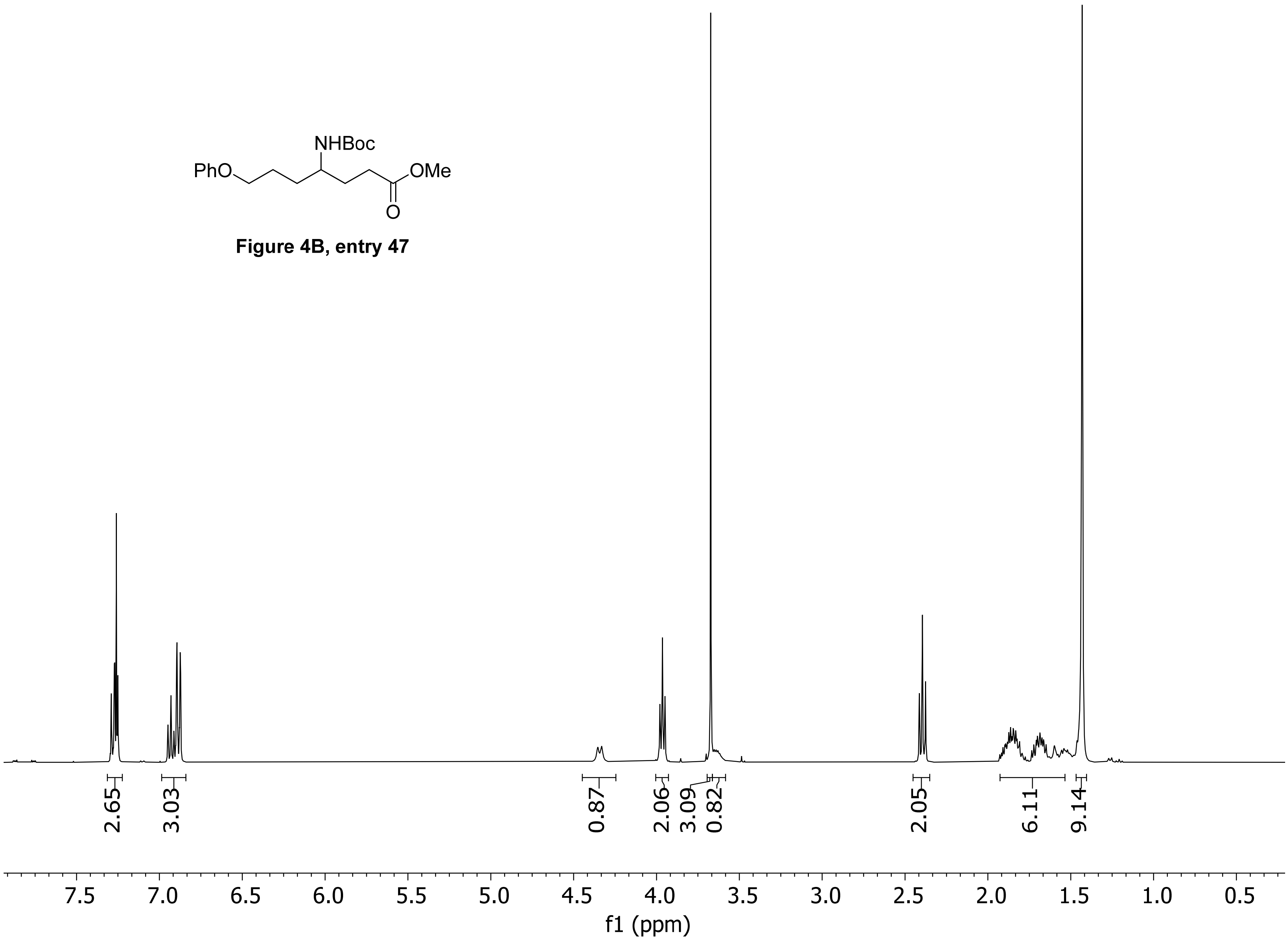


Figure 4B, entry 46


NHBoc
PhO
OMe
O
Figure 4B, entry 47
2.65
3.03
0.87
2.06
3.09
0.82
2.05
6.11
9.14
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

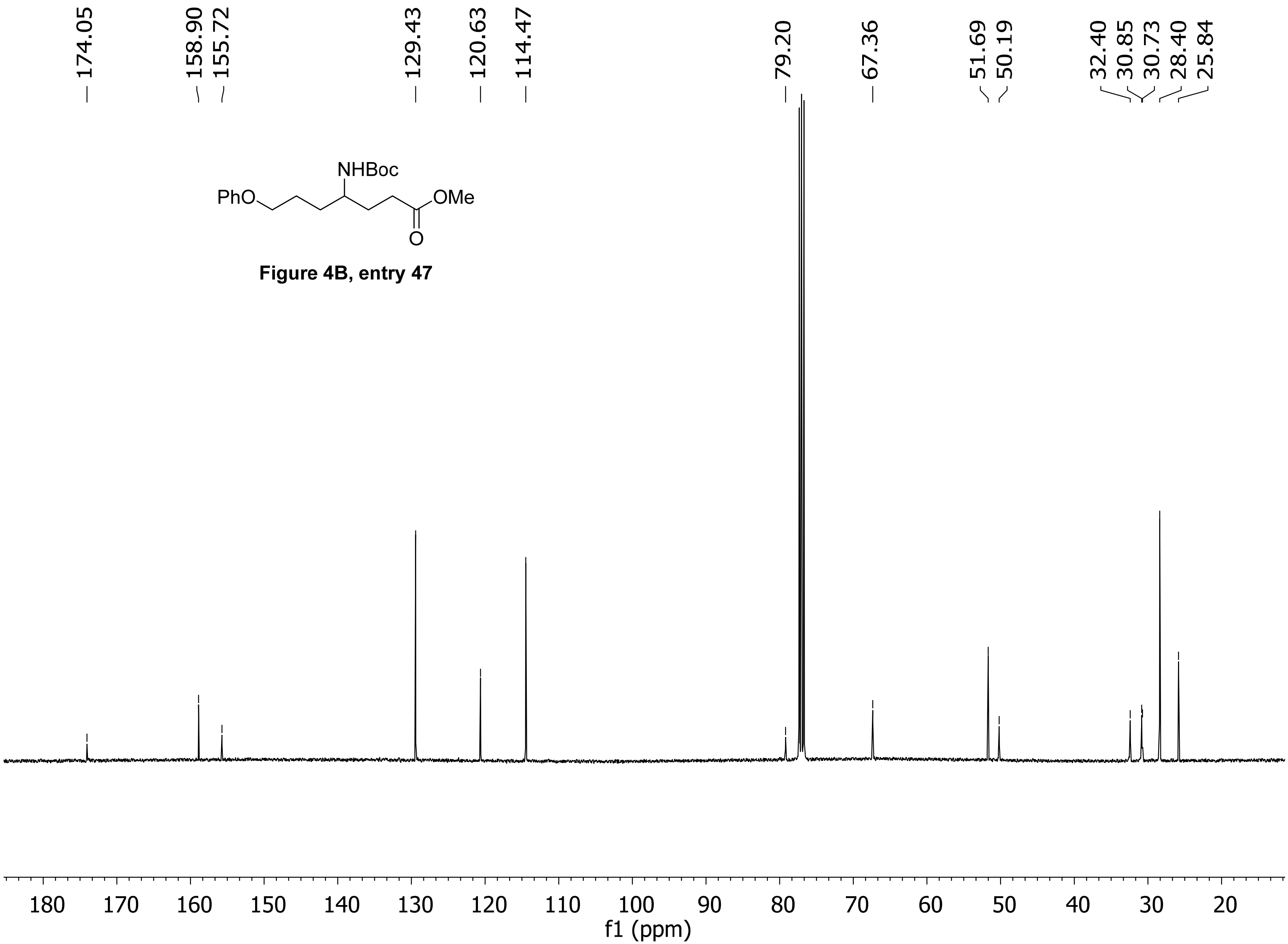
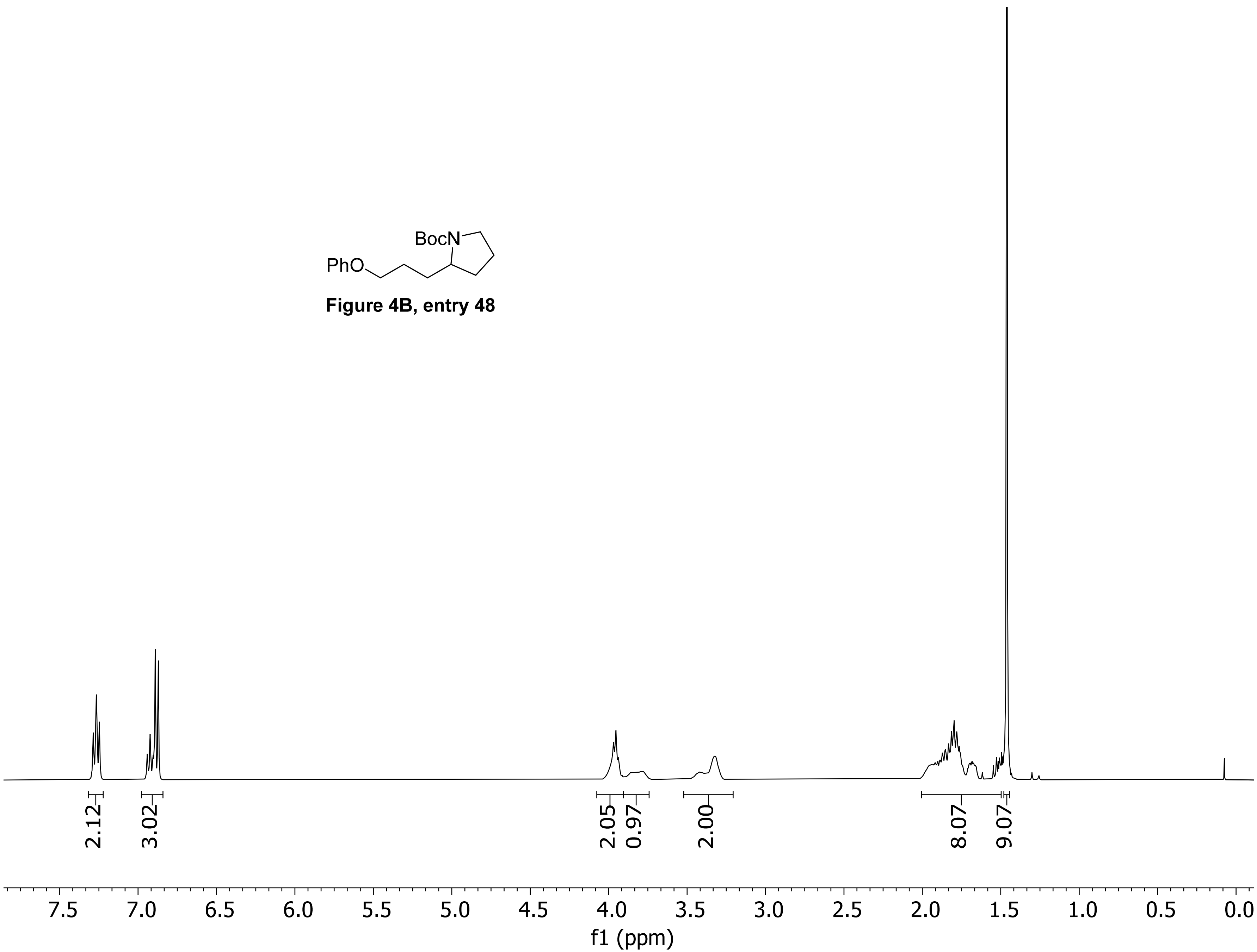


Figure 4B, entry 47



BocN
PhO
Figure 4B, entry 48
2.12
3.02
2.05
0.97
2.00
8.07
9.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

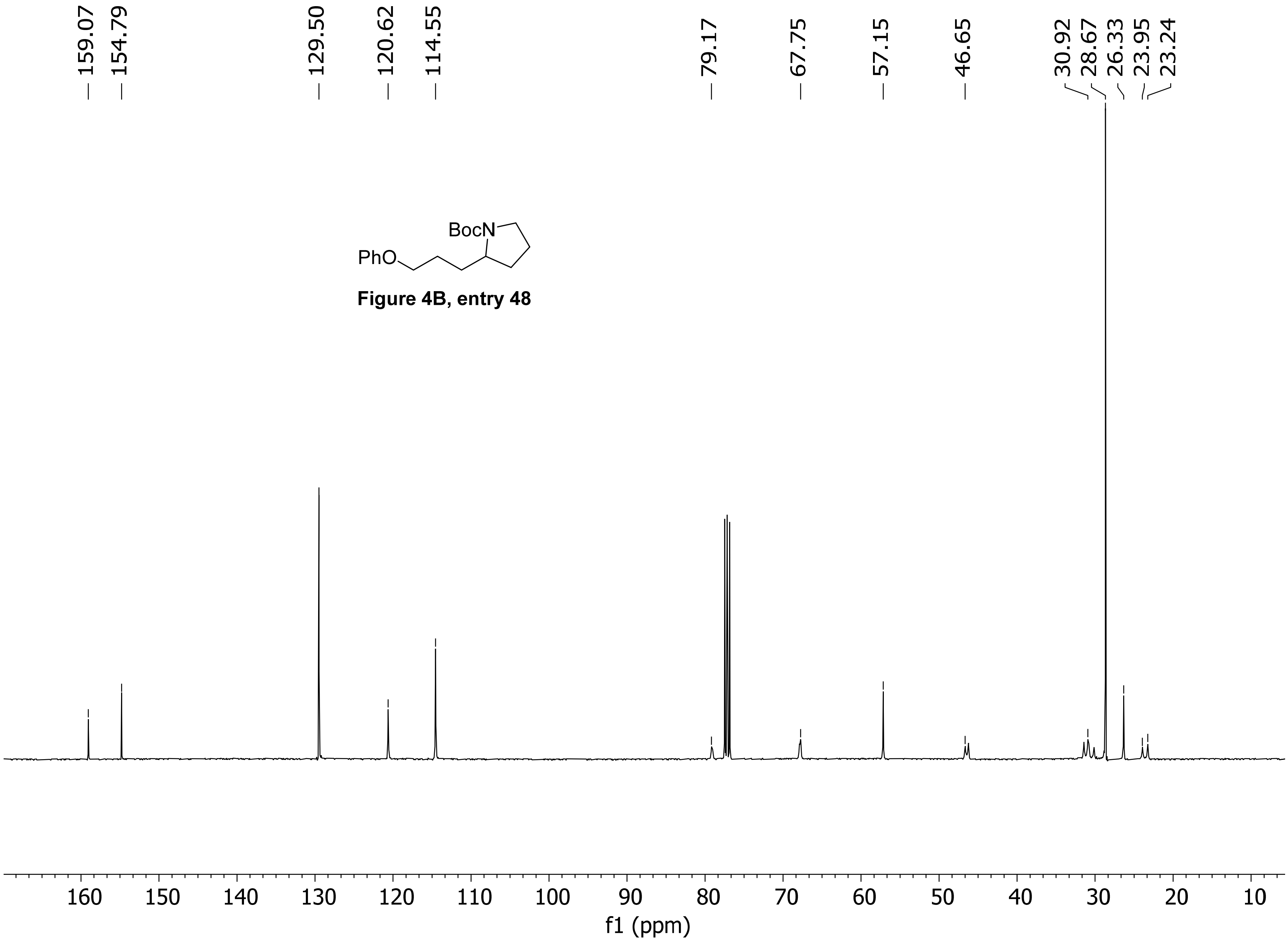
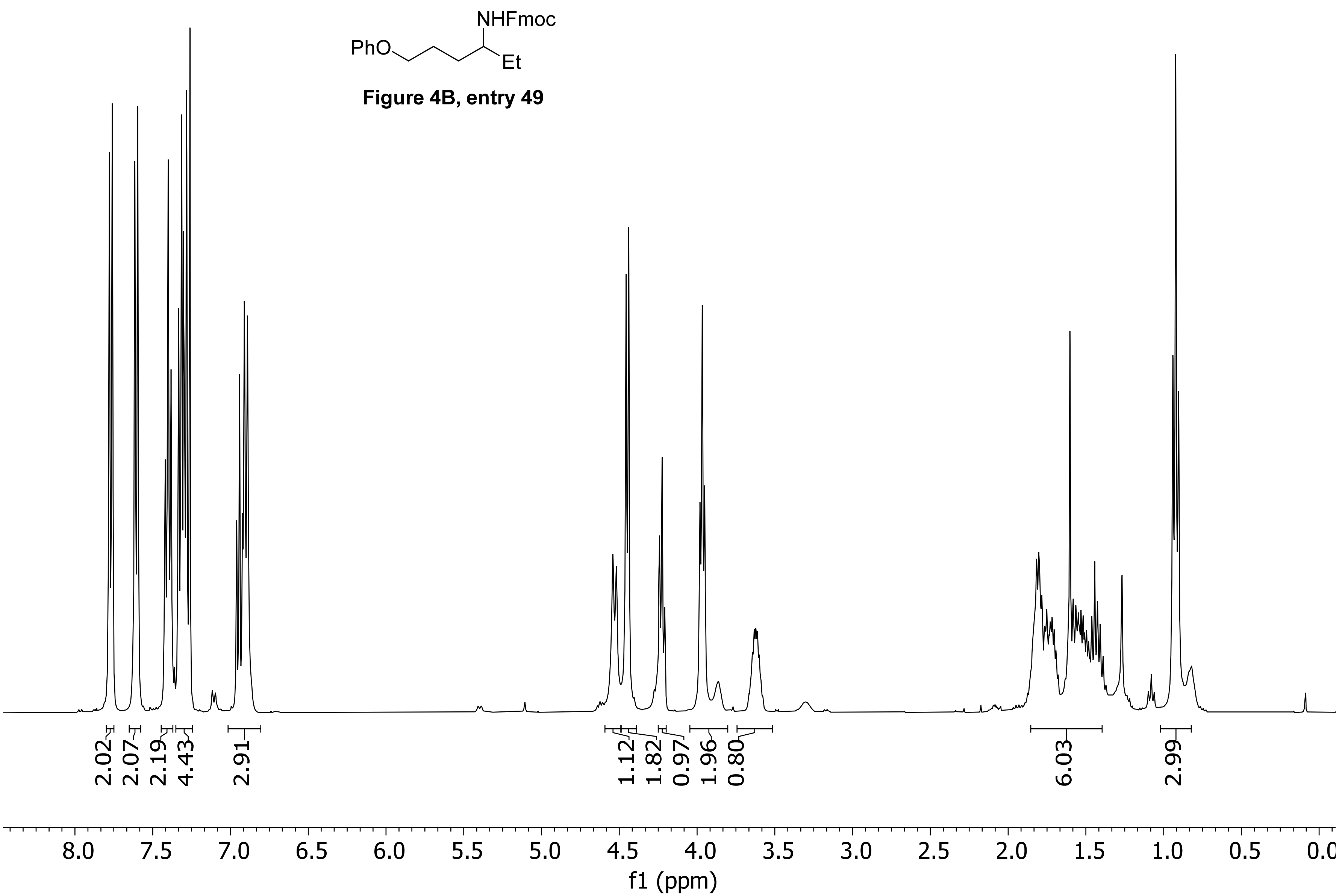
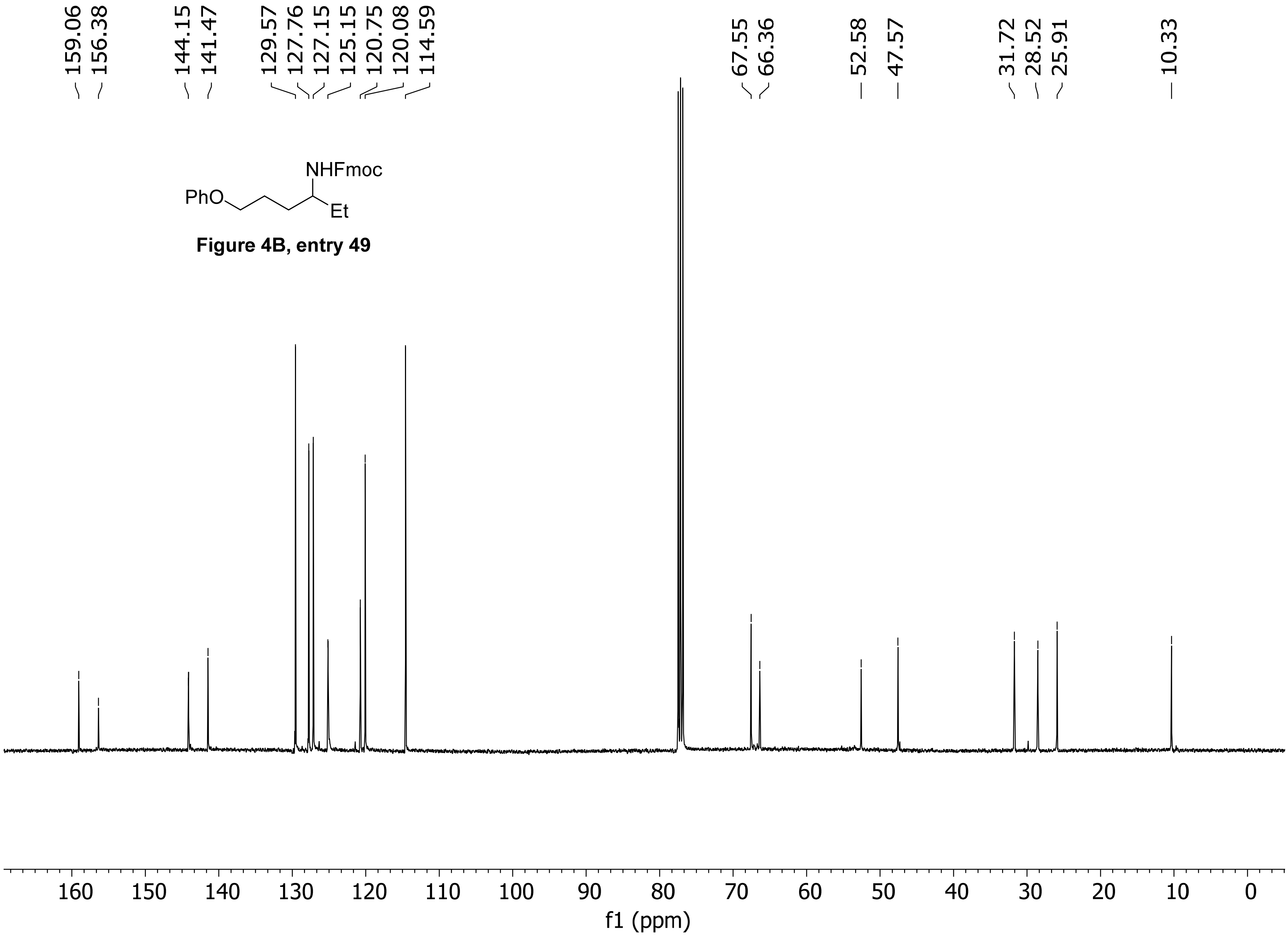
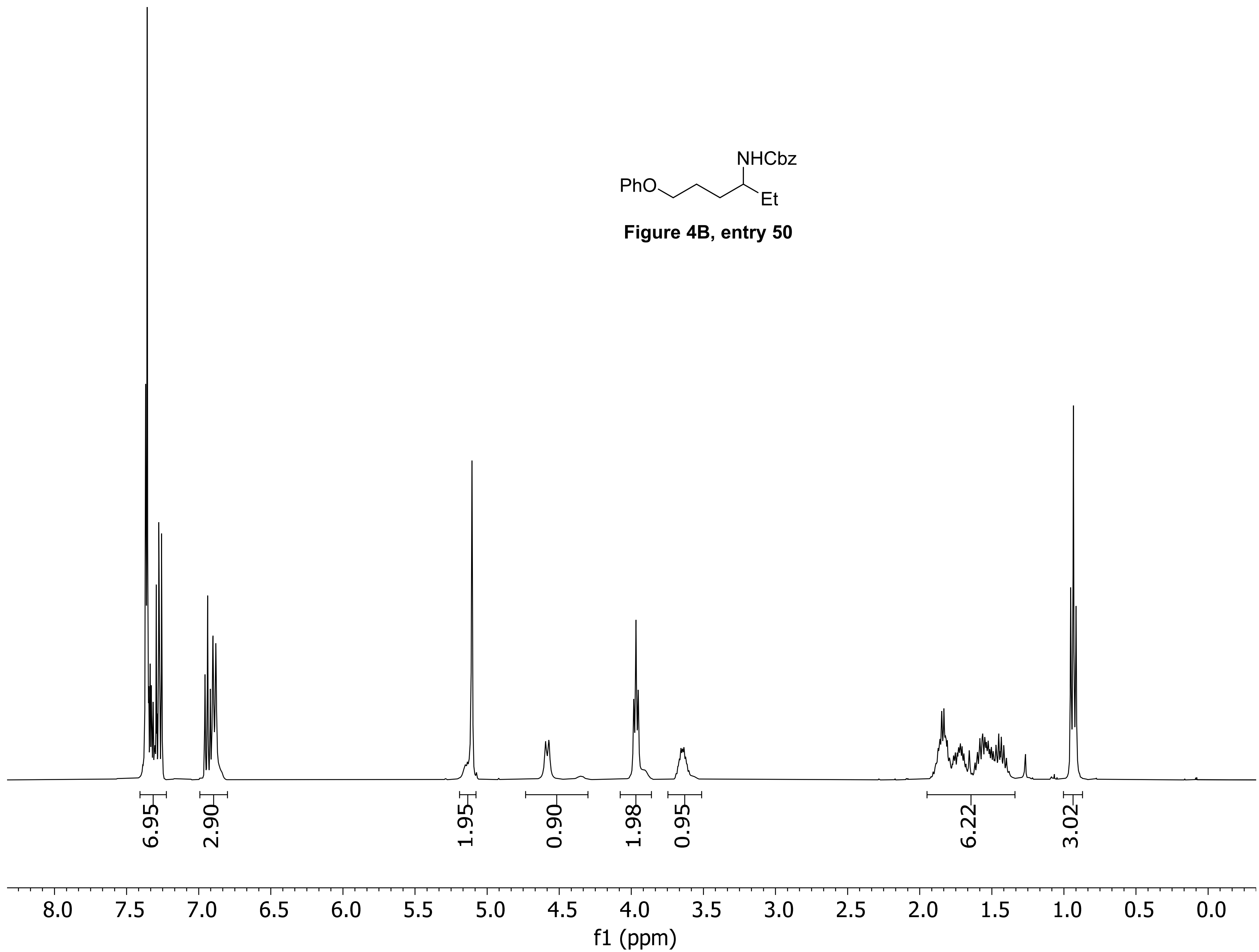


Figure 4B, entry 48


NHFmoc
PhO
Et
Figure 4B, entry 49
2.02
2.07
2.19
4.43
2.91
1.12
1.82
0.97
1.96
0.80
6.03
2.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



159.06
156.38
144.15
141.47
129.57
127.76
127.15
125.15
120.75
120.08
114.59
67.55
66.36
52.58
47.57
31.72
28.52
25.91
10.33
NHFmoc
PhO
Et
Figure 4B, entry 49
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NHCbz
PhO
Et
Figure 4B, entry 50
6.95
2.90
1.95
0.90
1.98
0.95
6.22
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

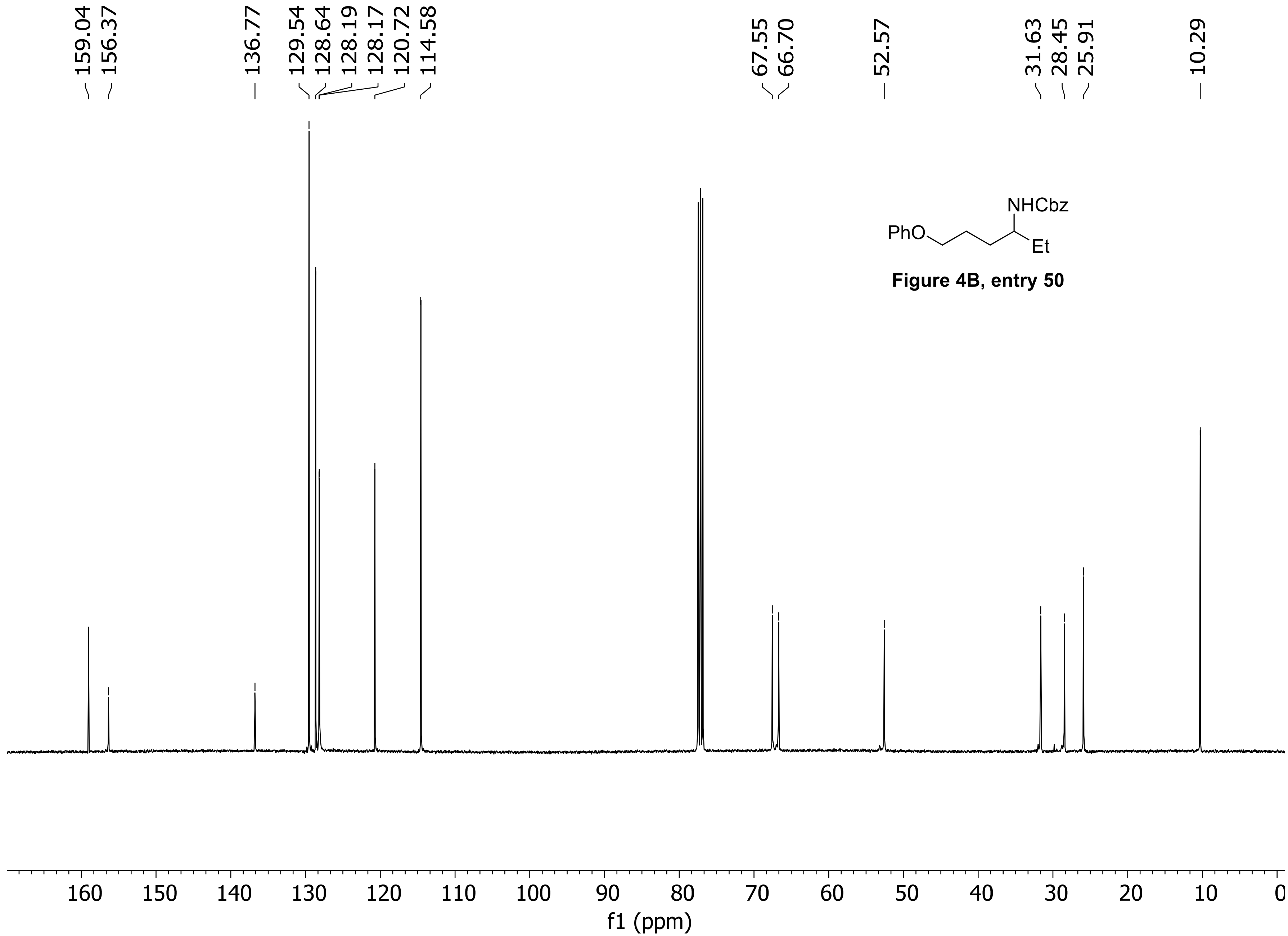


Figure 4B, entry 50

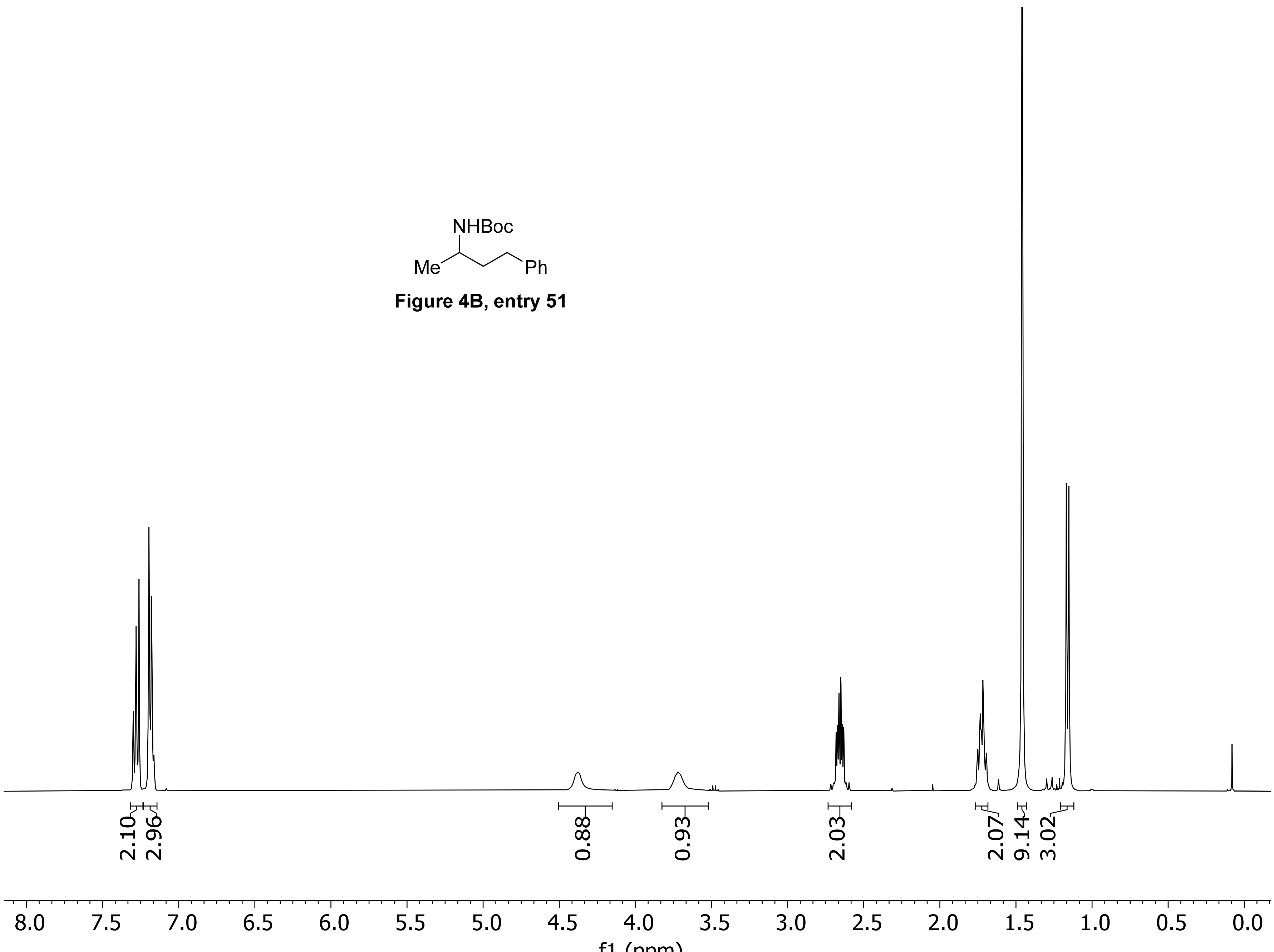
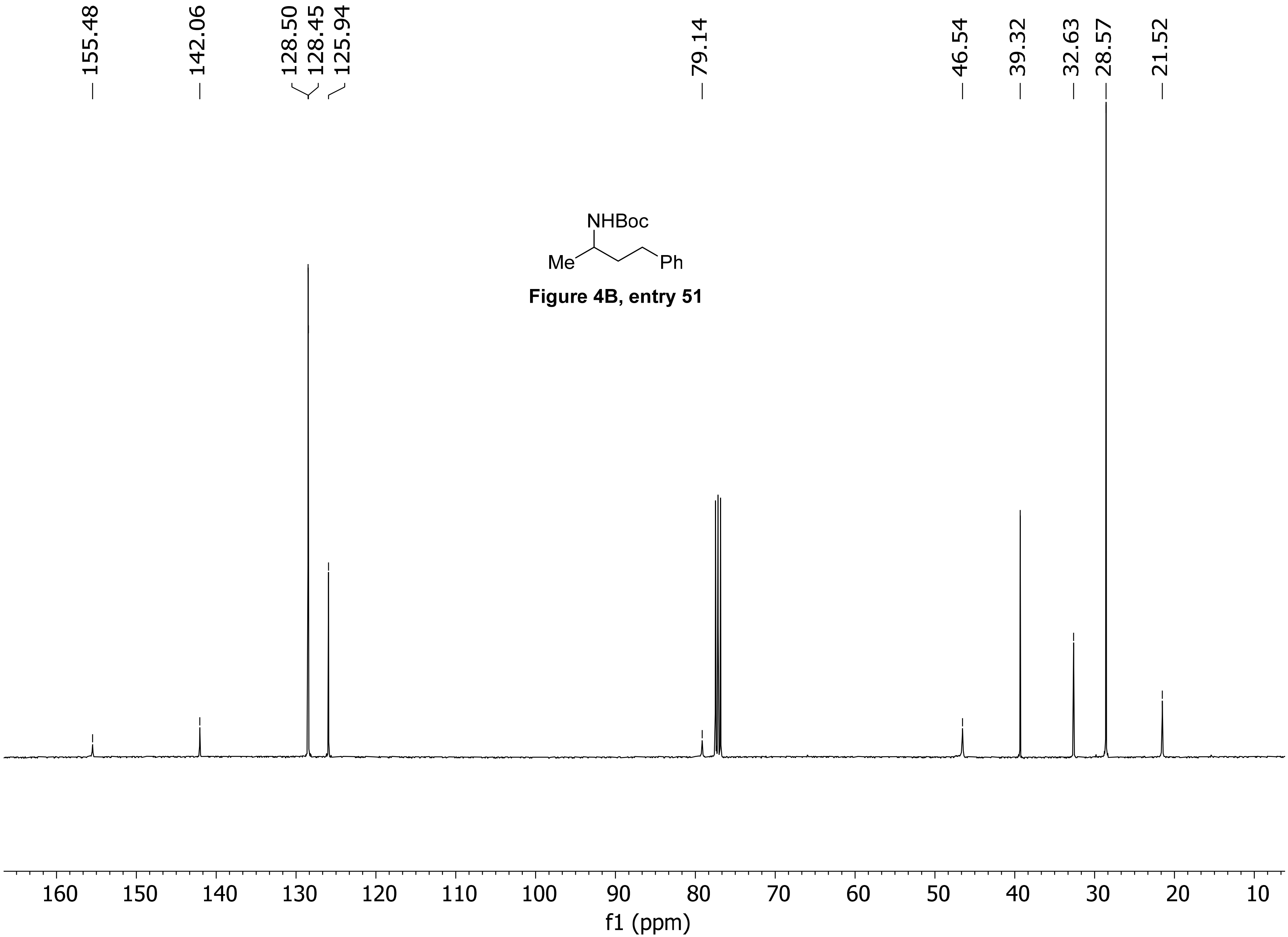


Figure 4B, entry 51


155.48
142.06
128.50
128.45
125.94
79.14
46.54
39.32
32.63
28.57
21.52
NHBoc
Me
Ph
Figure 4B, entry 51
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

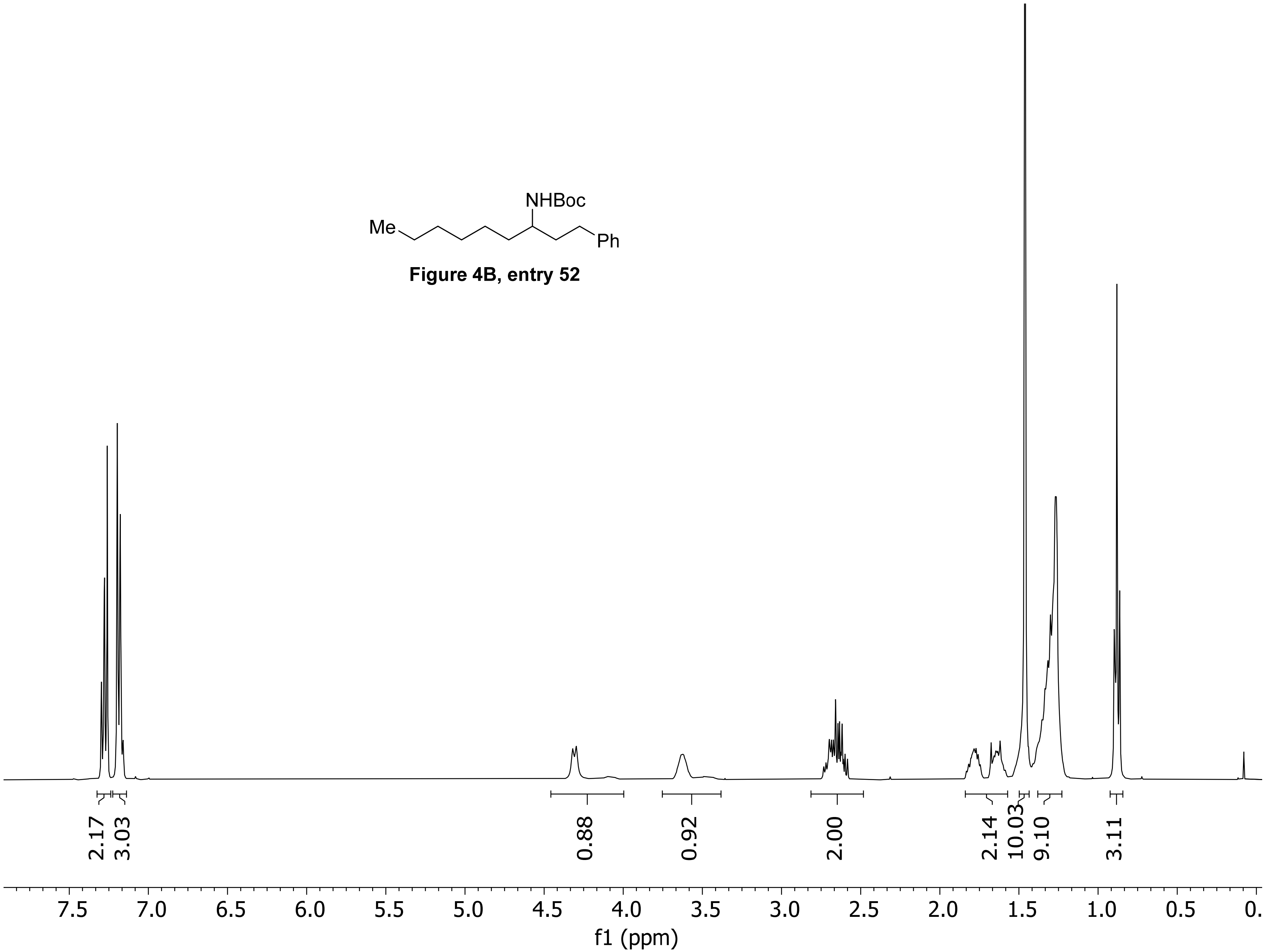
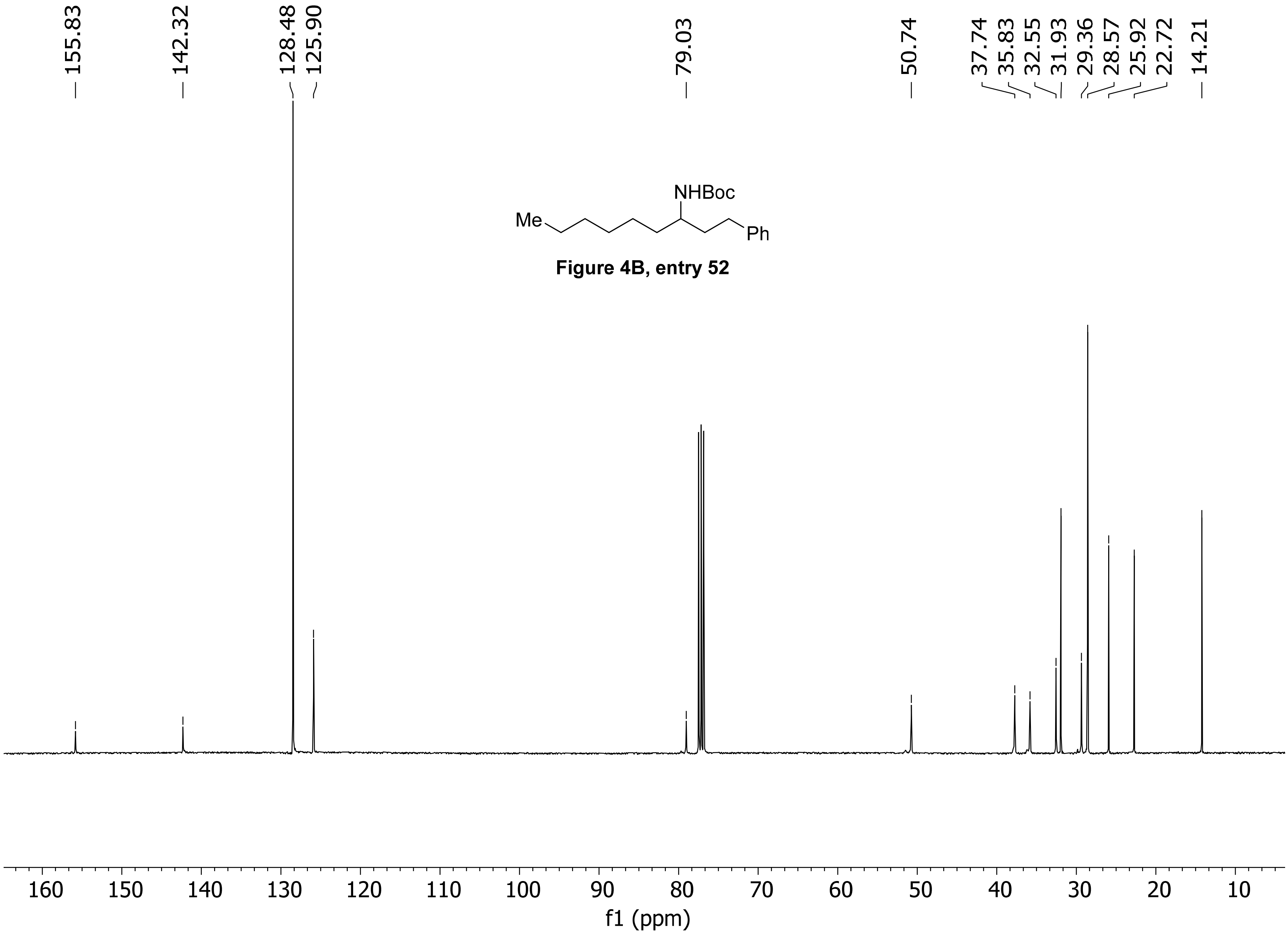
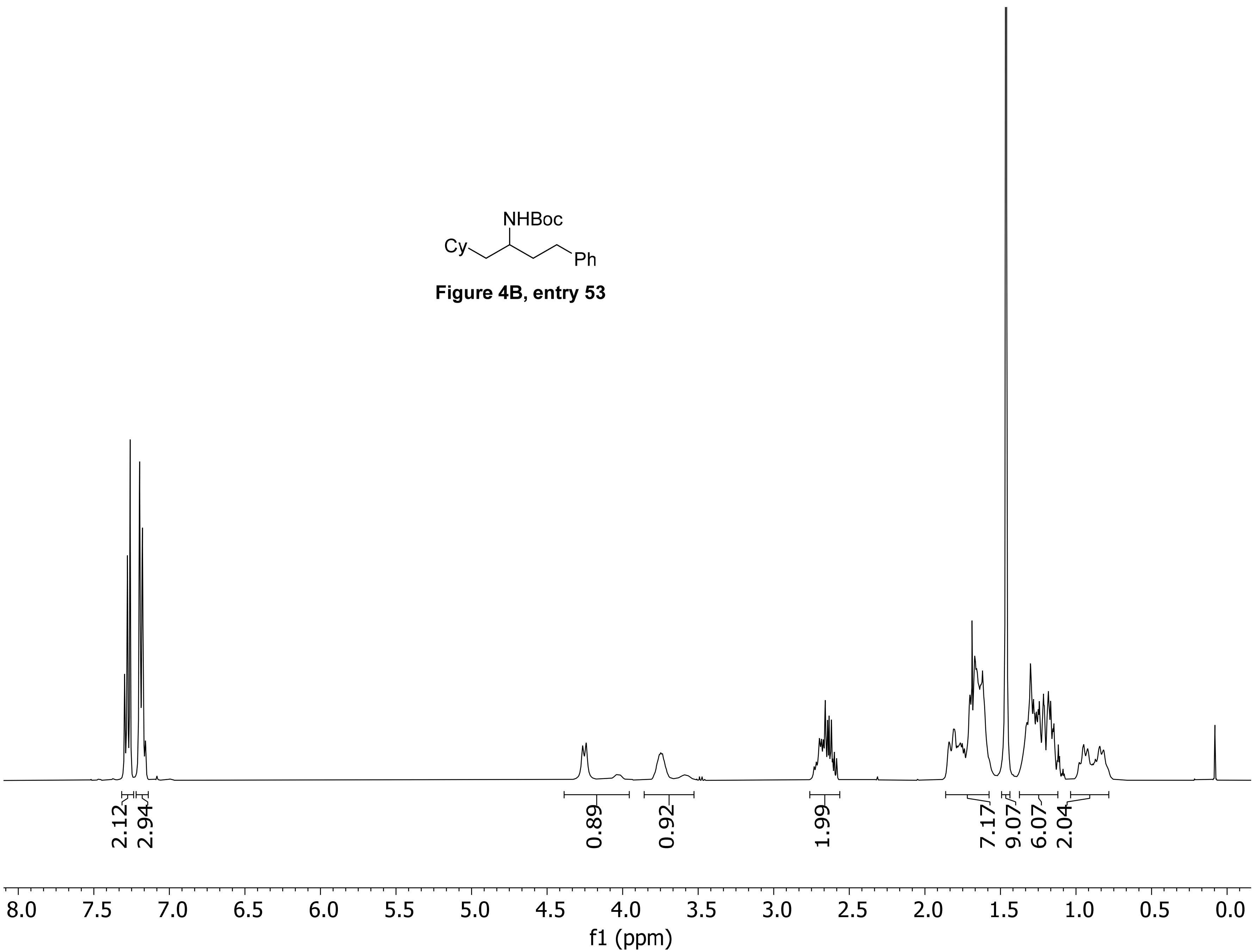


Figure 4B, entry 52


155.83
142.32
128.48
125.90
79.03
50.74
37.74
35.83
32.55
31.93
29.36
28.57
25.92
22.72
14.21
NHBoc
Me
Ph
Figure 4B, entry 52
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


NHBoc
Cy
Ph
Figure 4B, entry 53
2.12
2.94
0.89
0.92
1.99
7.17
9.07
6.07
2.04
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

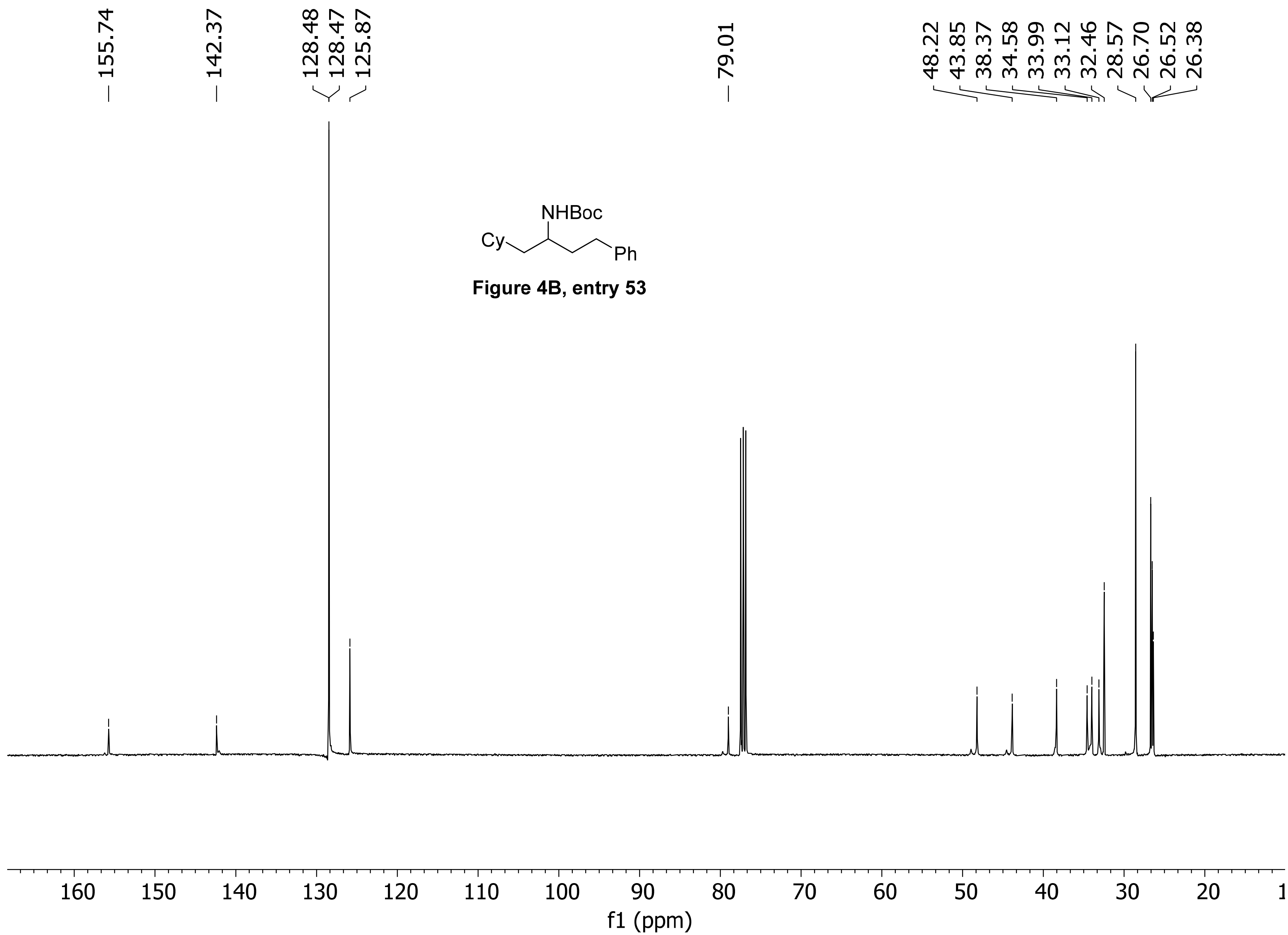


Figure 4B, entry 53

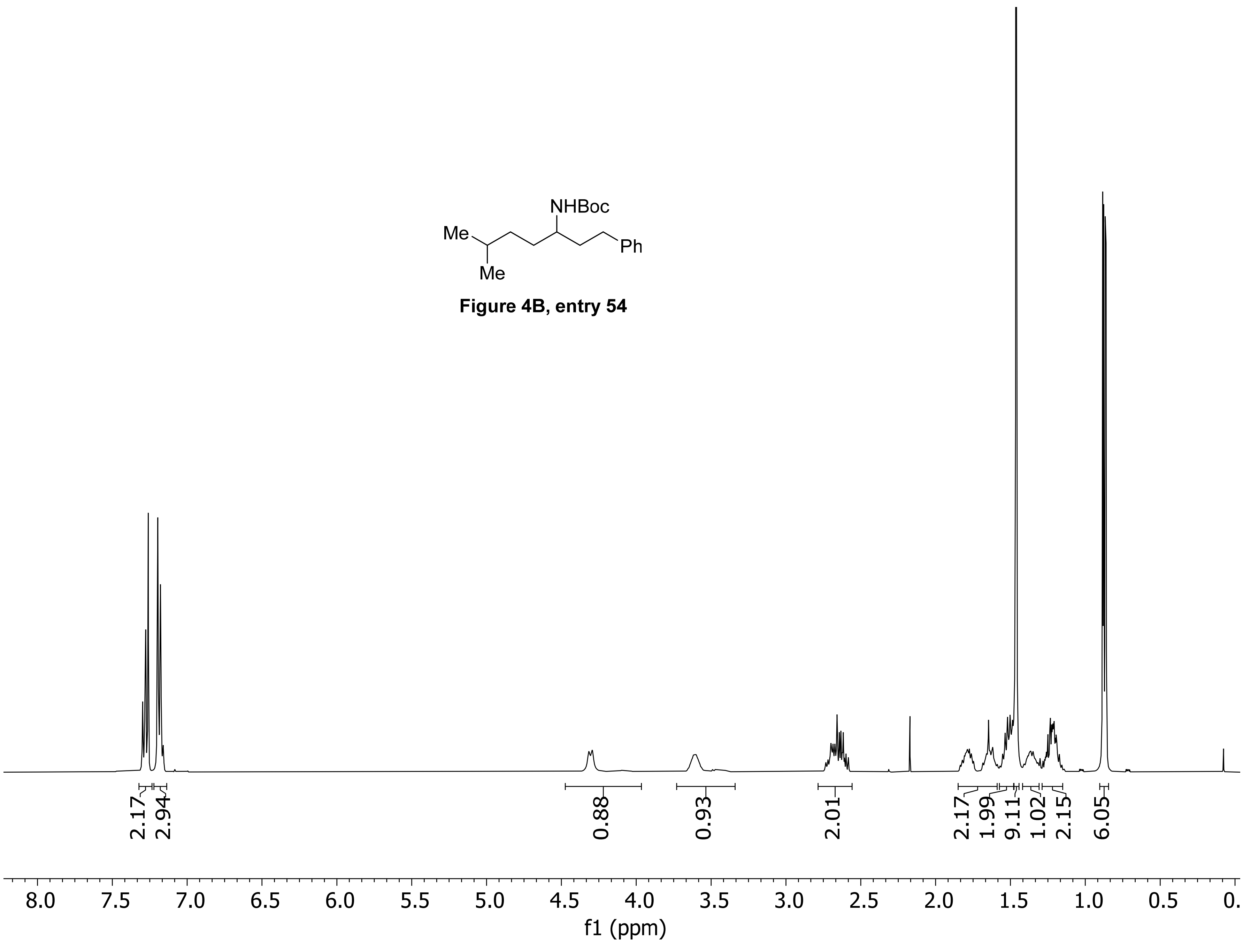
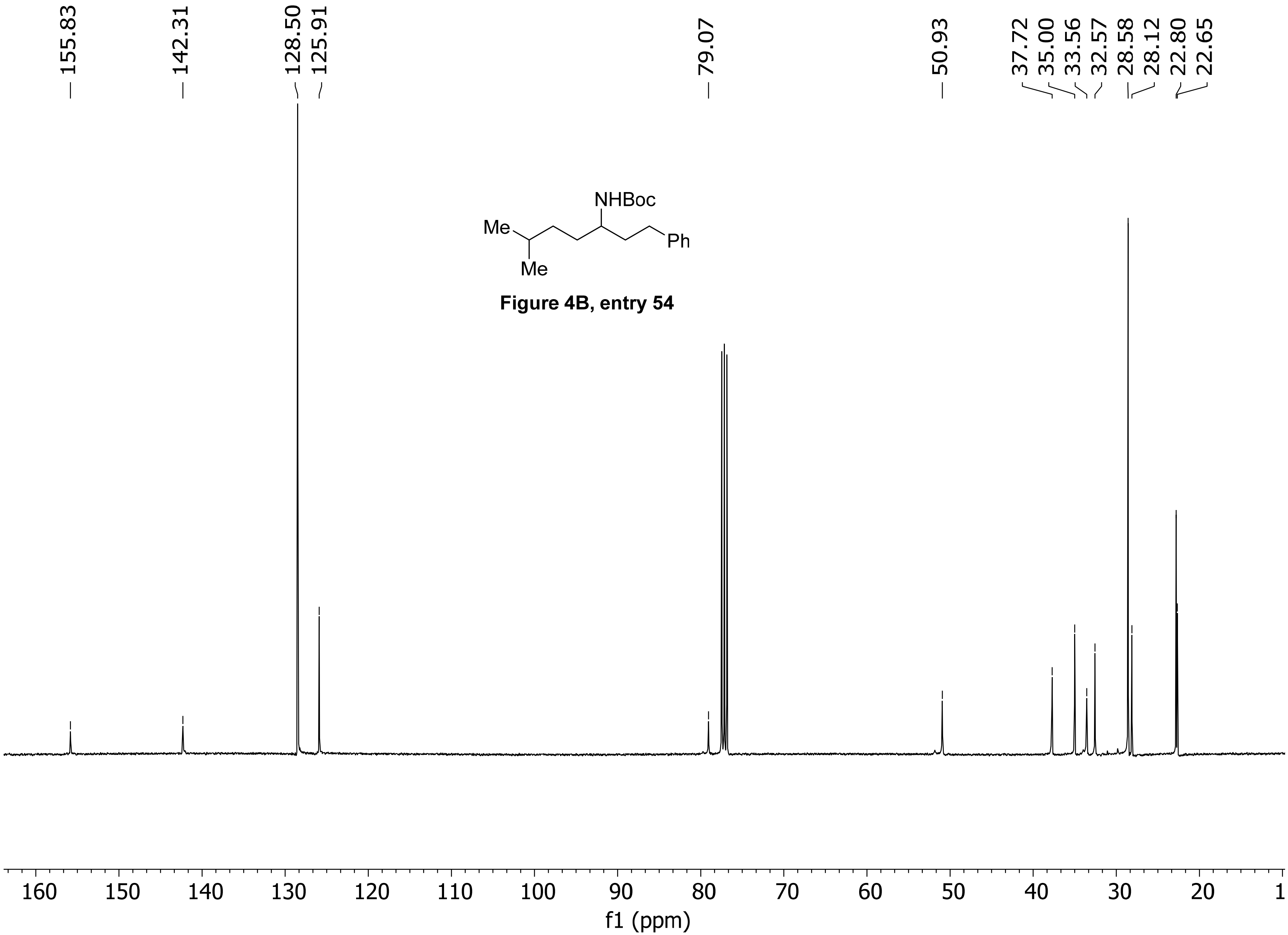
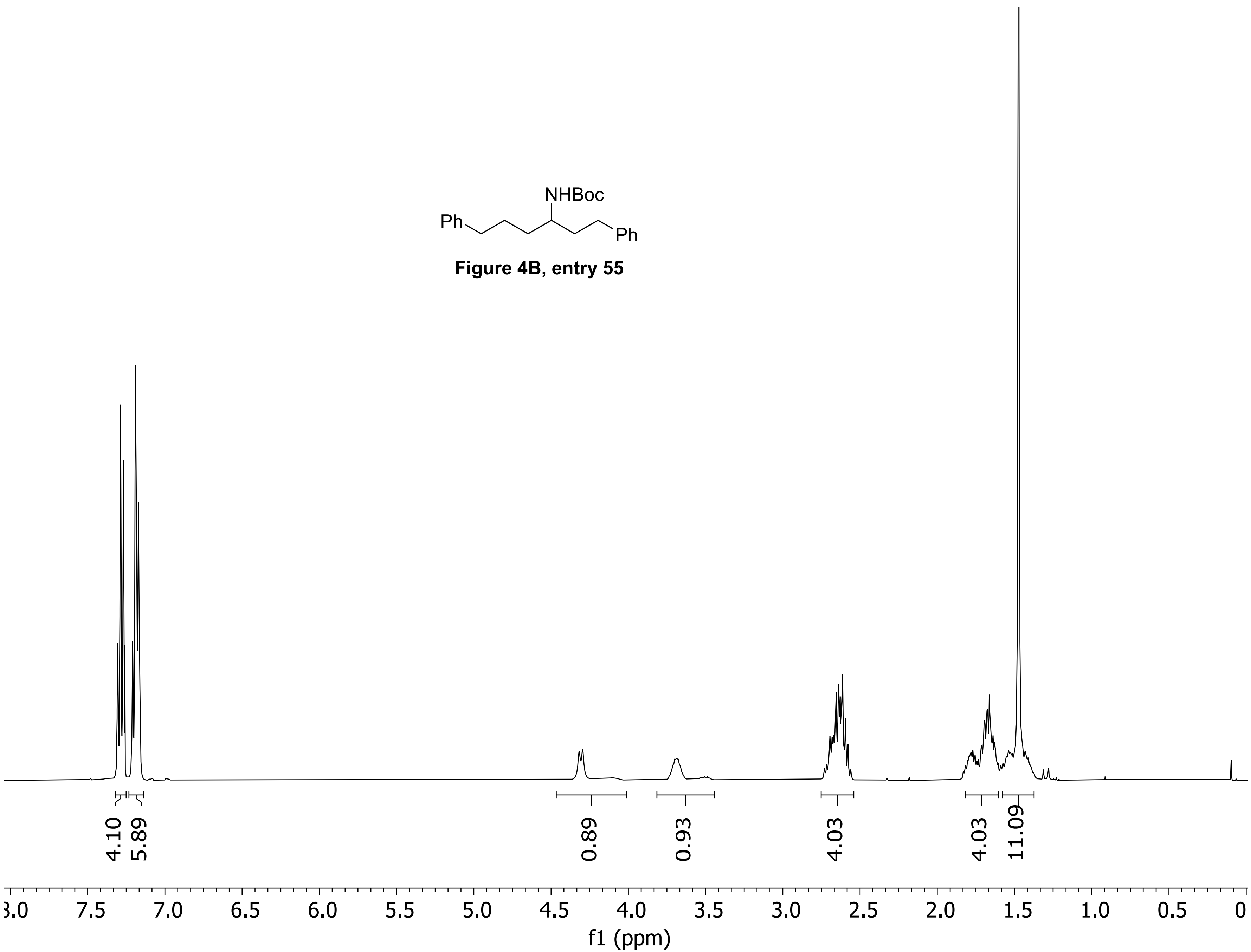
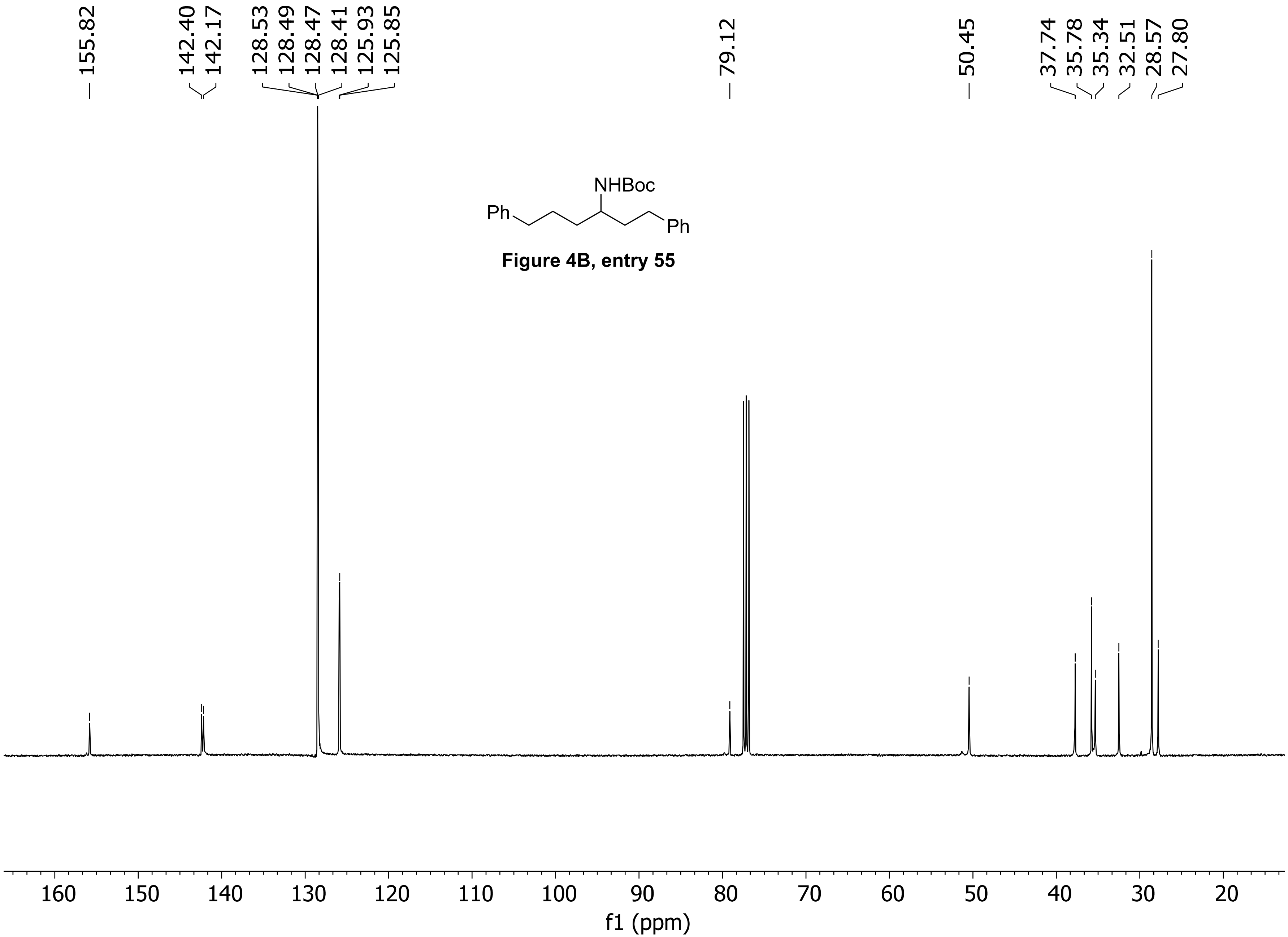


Figure 4B, entry 54


155.83
142.31
128.50
125.91
79.07
50.93
37.72
35.00
33.56
32.57
28.58
28.12
22.80
22.65
NHBoc
Me
Ph
Me
Figure 4B, entry 54
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



NHBoc
Ph
Ph
Figure 4B, entry 55
4.10
5.89
0.89
0.93
4.03
4.03
11.09
f1 (ppm)


155.82
142.40
142.17
128.53
128.49
128.47
128.41
125.93
125.85
79.12
50.45
37.74
35.78
35.34
32.51
28.57
27.80
NHBoc
Ph
Ph
Figure 4B, entry 55
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

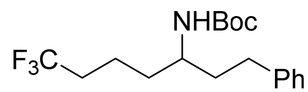
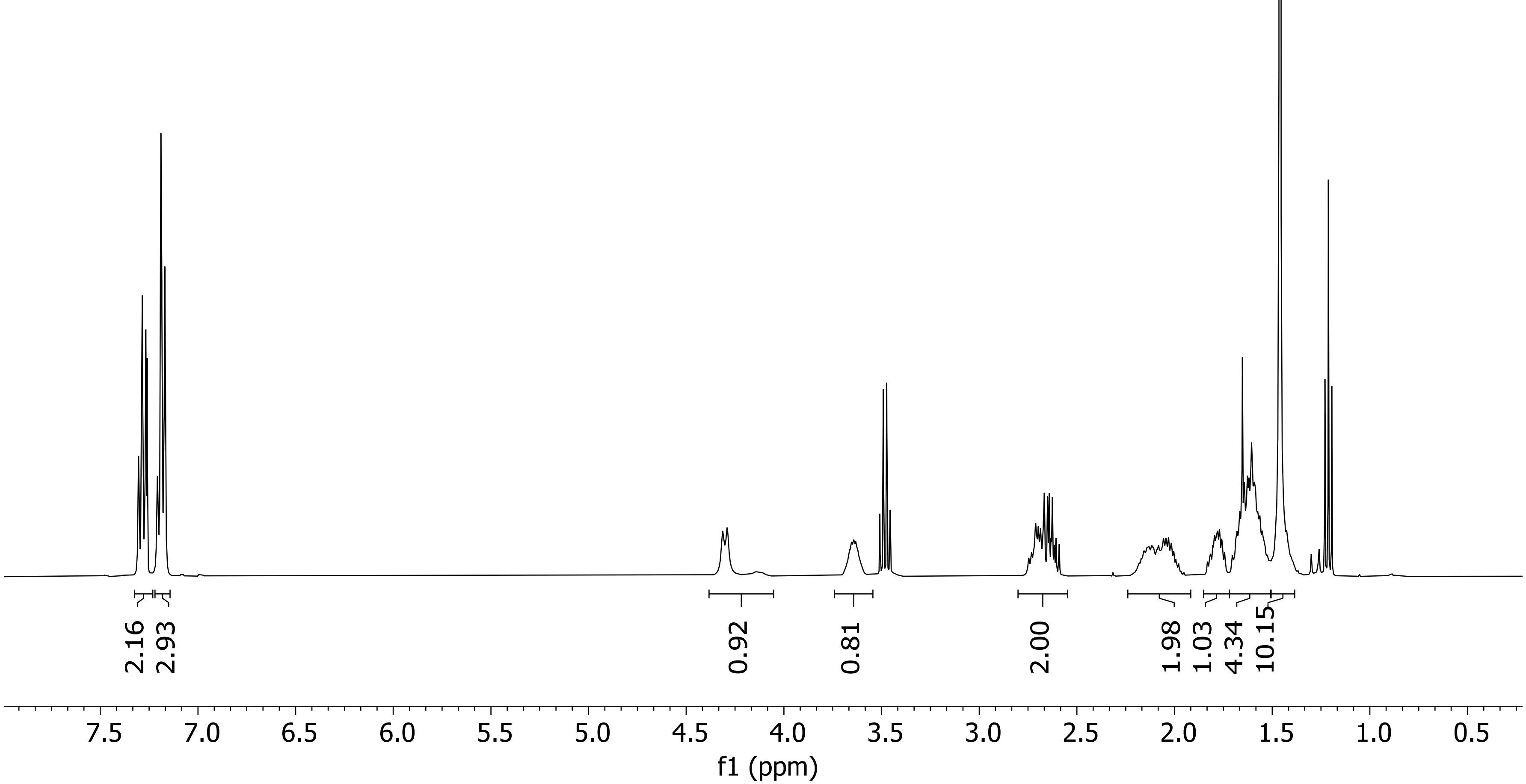


Figure 4B, entry 56



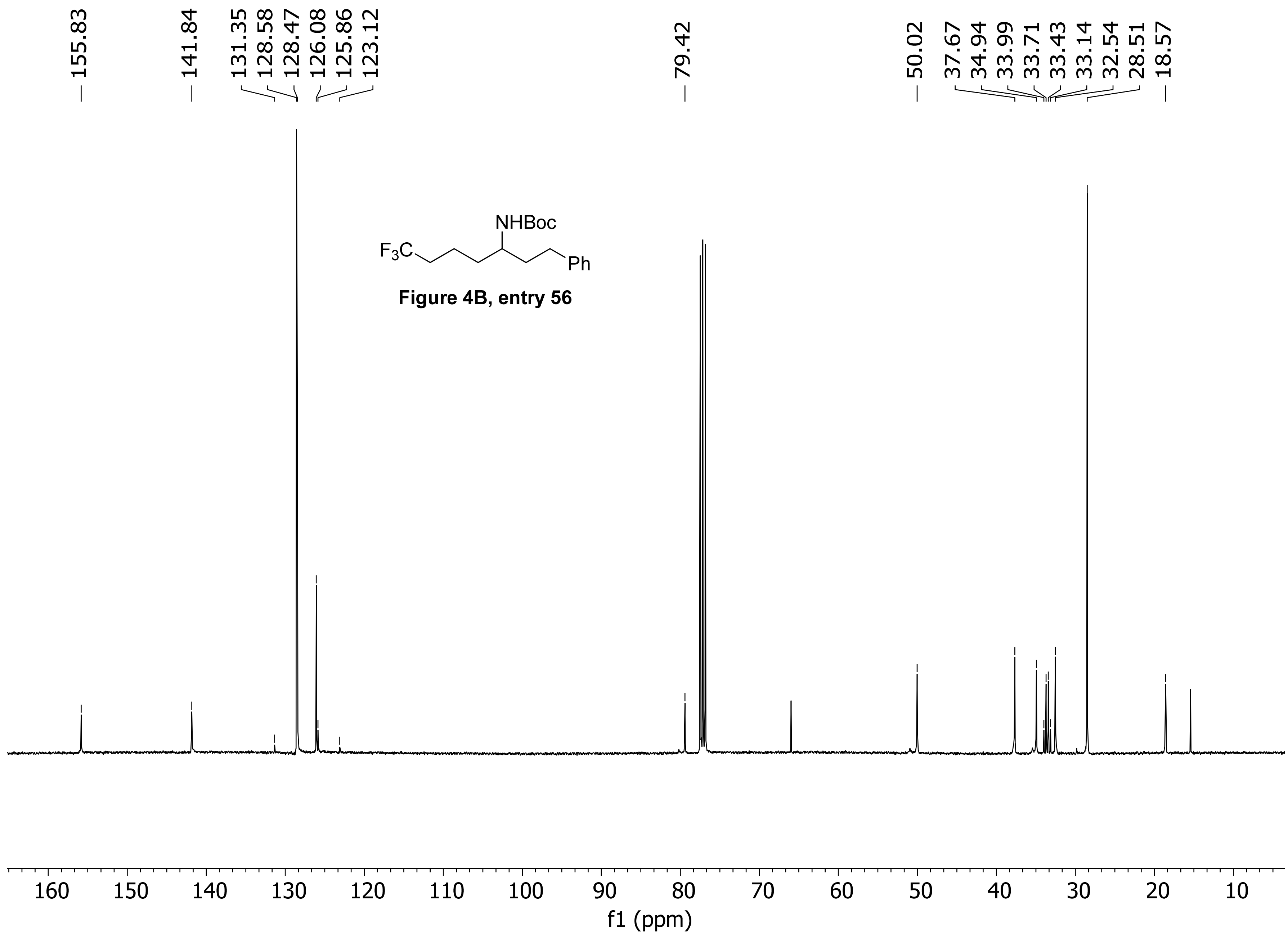


Figure 4B, entry 56

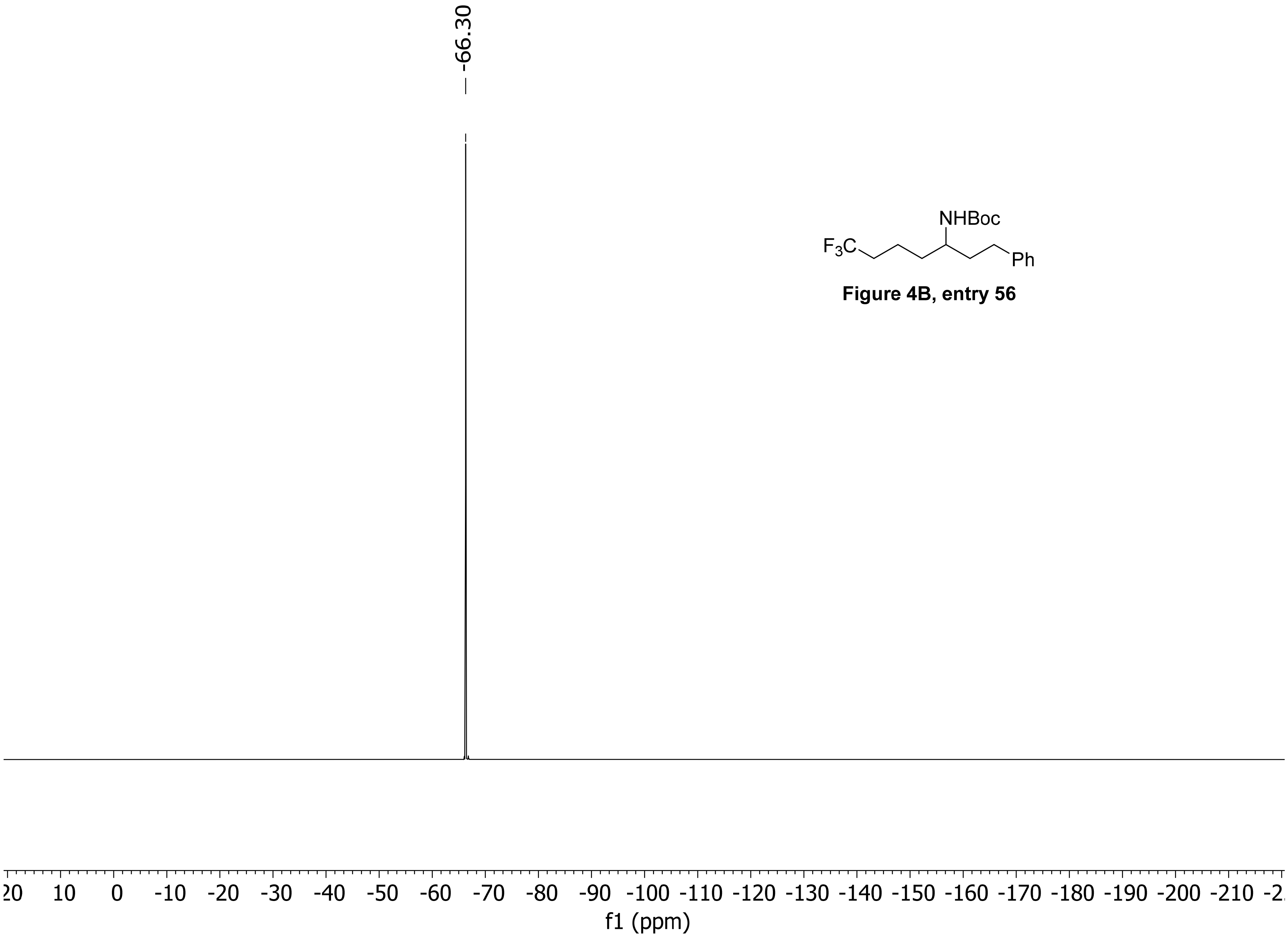


Figure 4B, entry 56

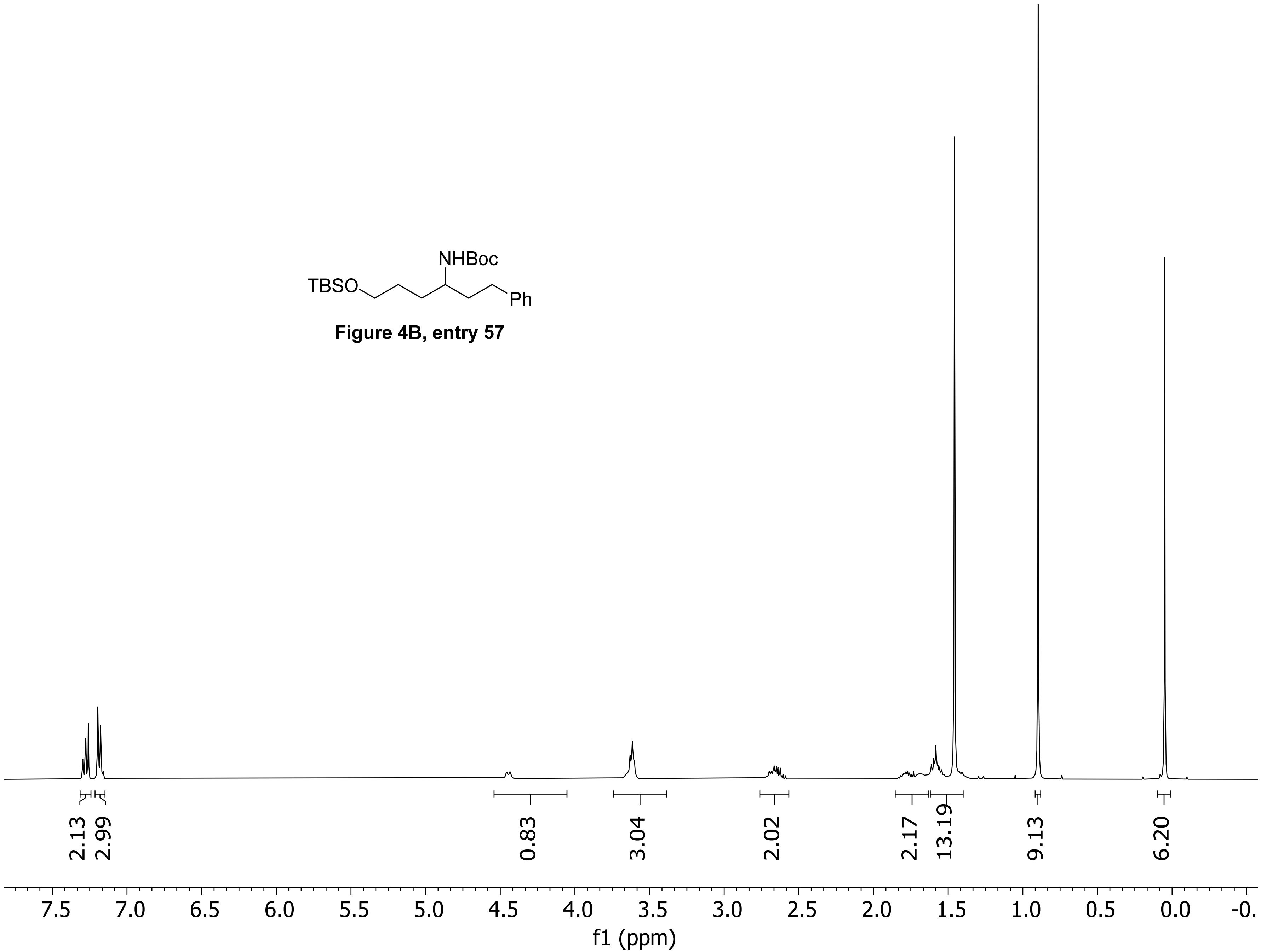


Figure 4B, entry 57

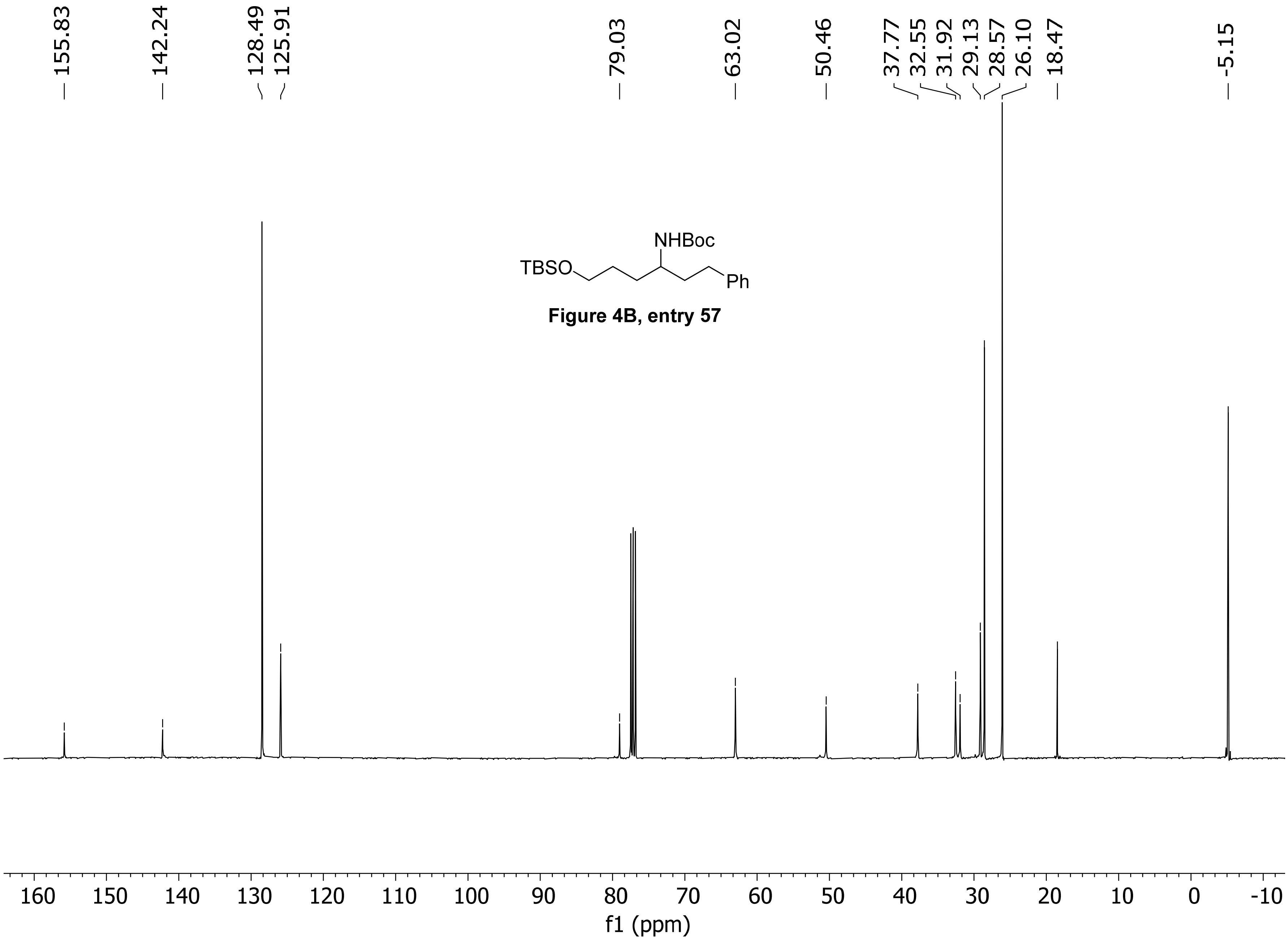


Figure 4B, entry 57

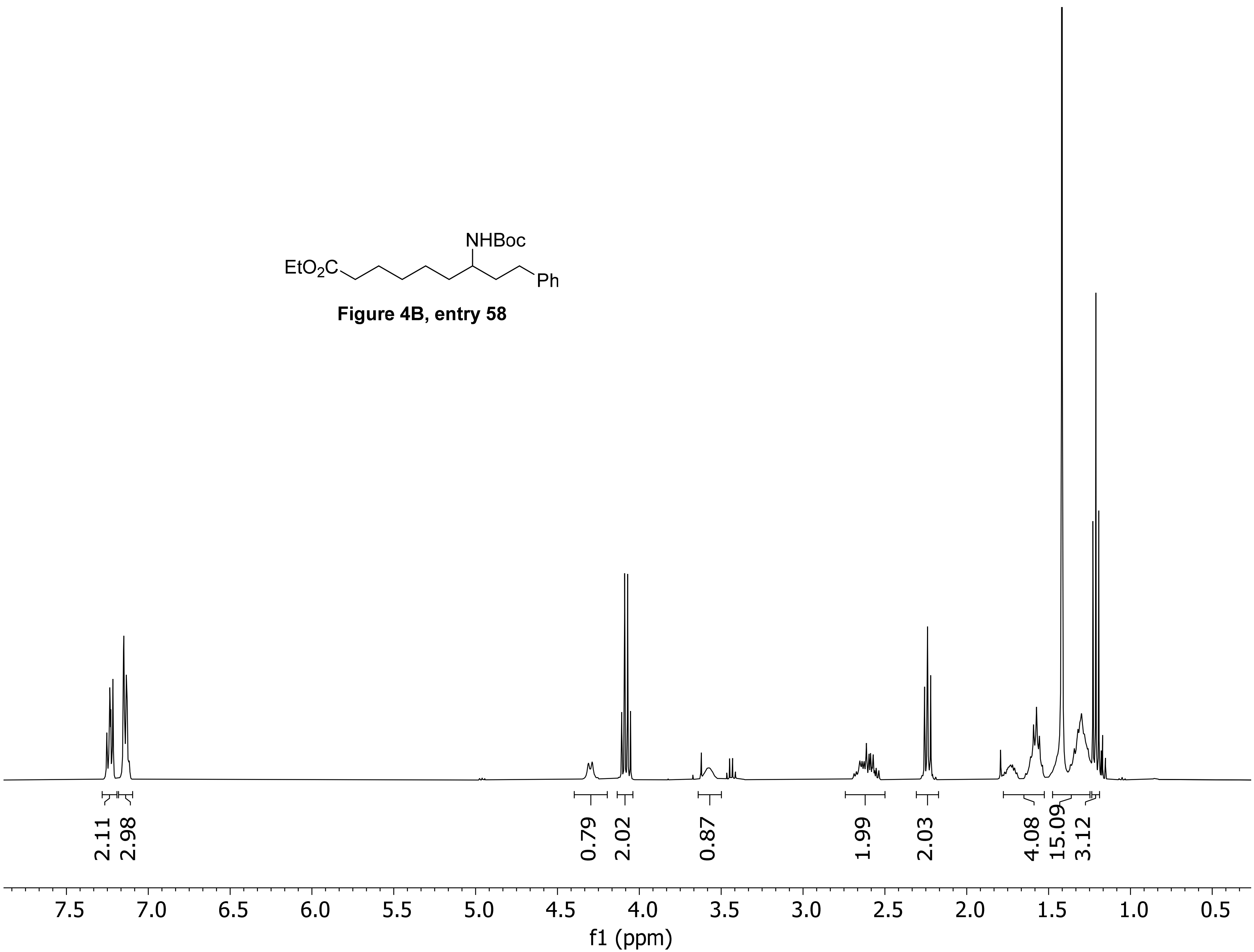


Figure 4B, entry 58

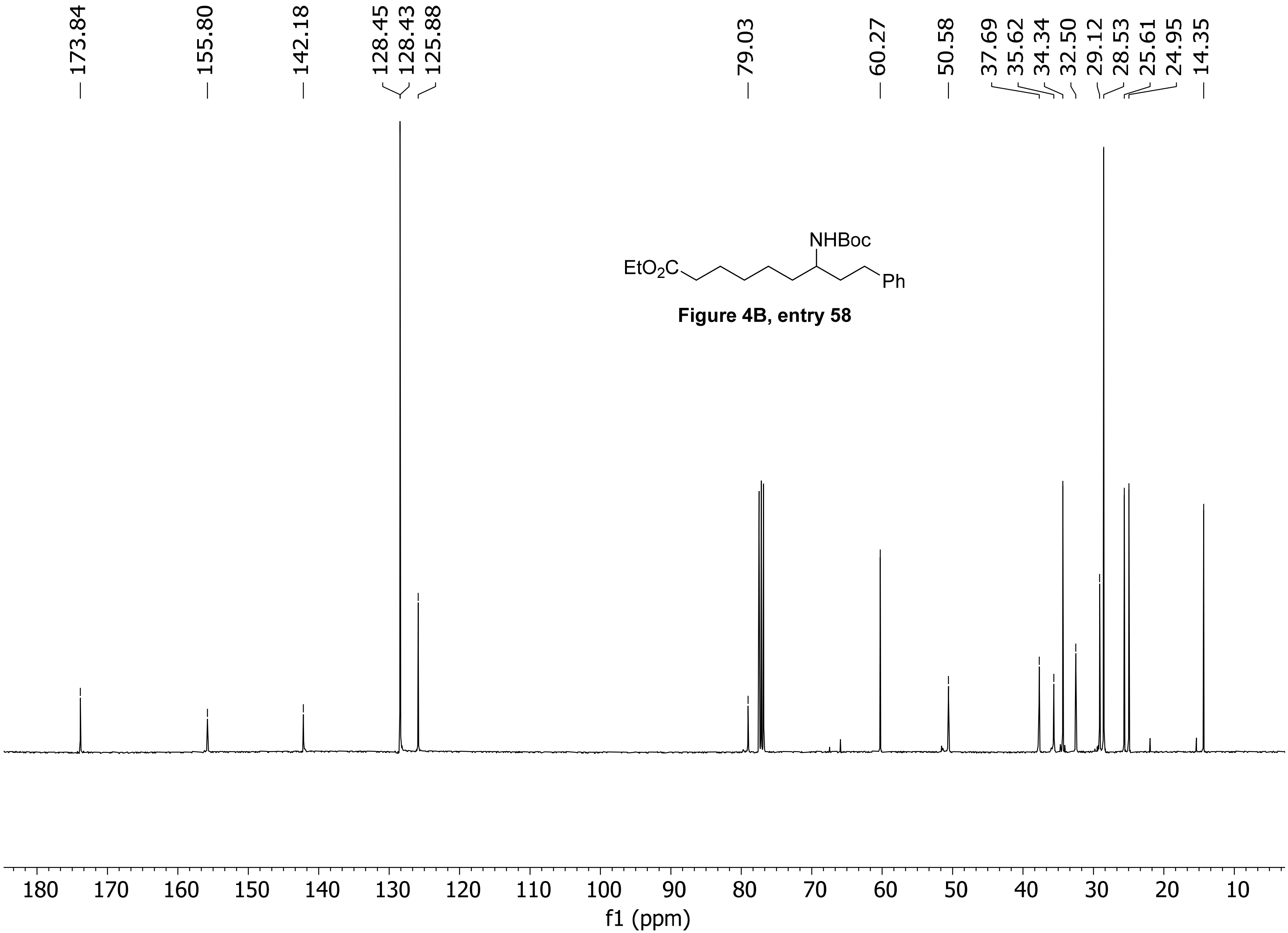


Figure 4B, entry 58

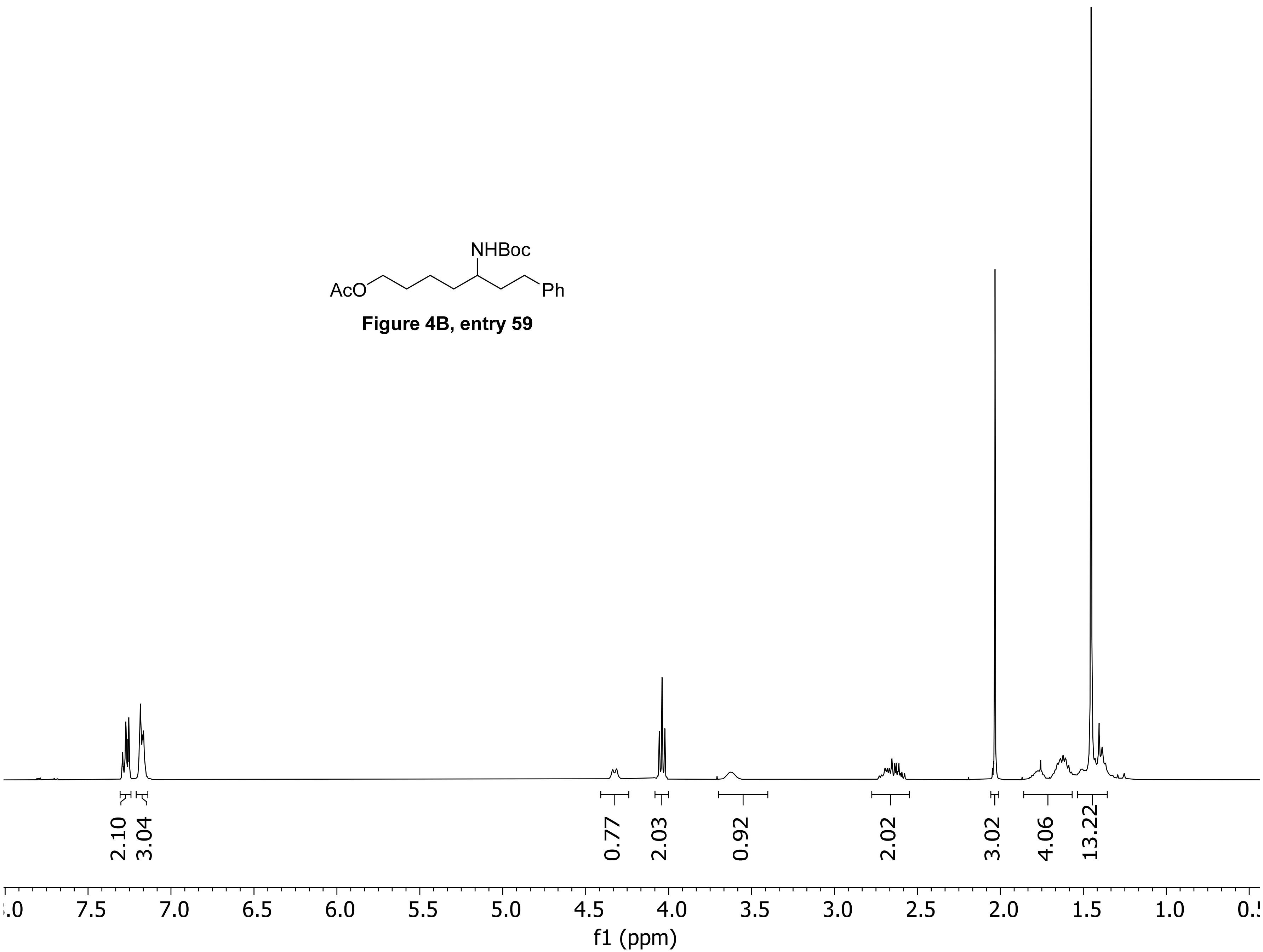


Figure 4B, entry 59

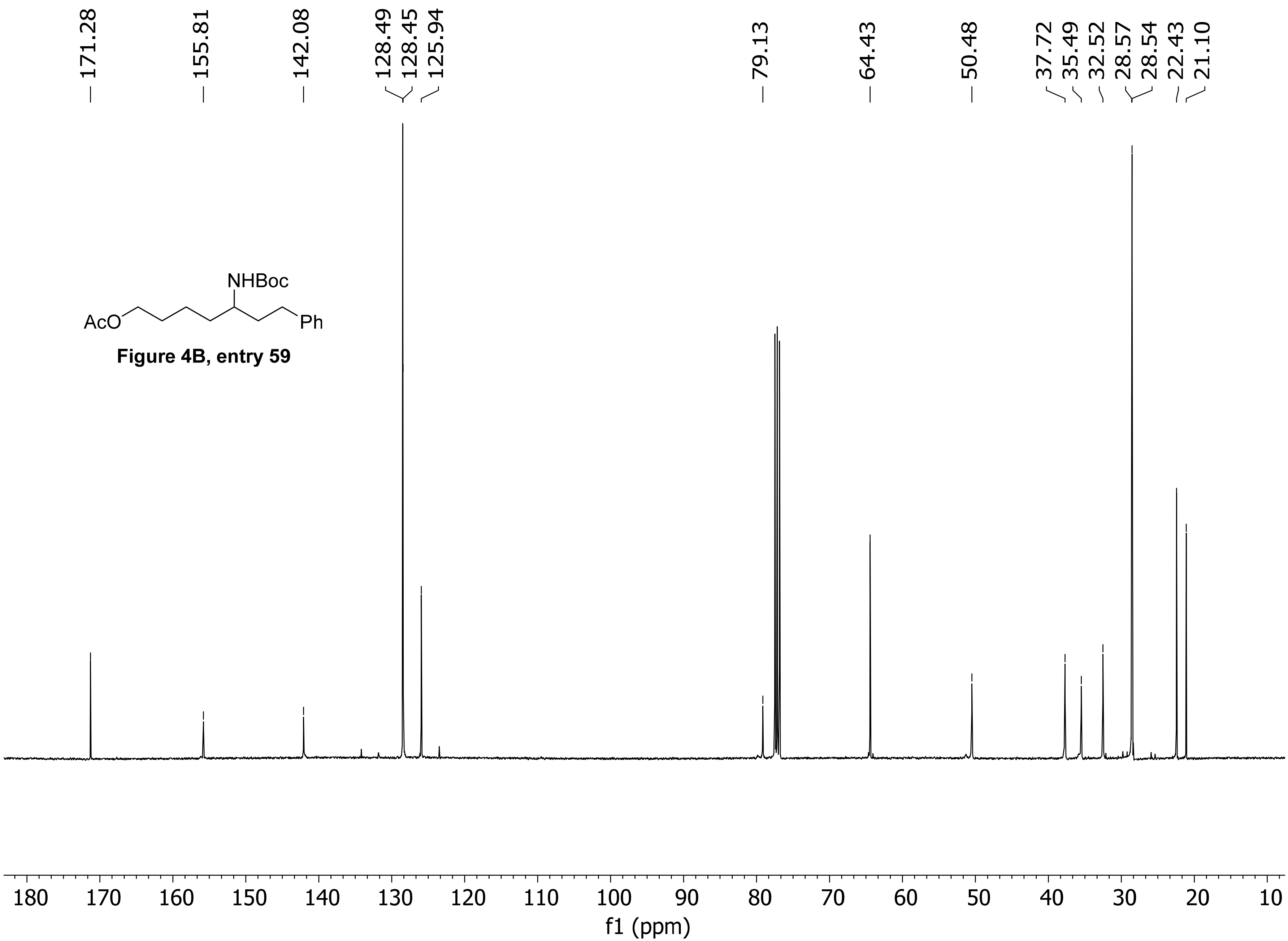
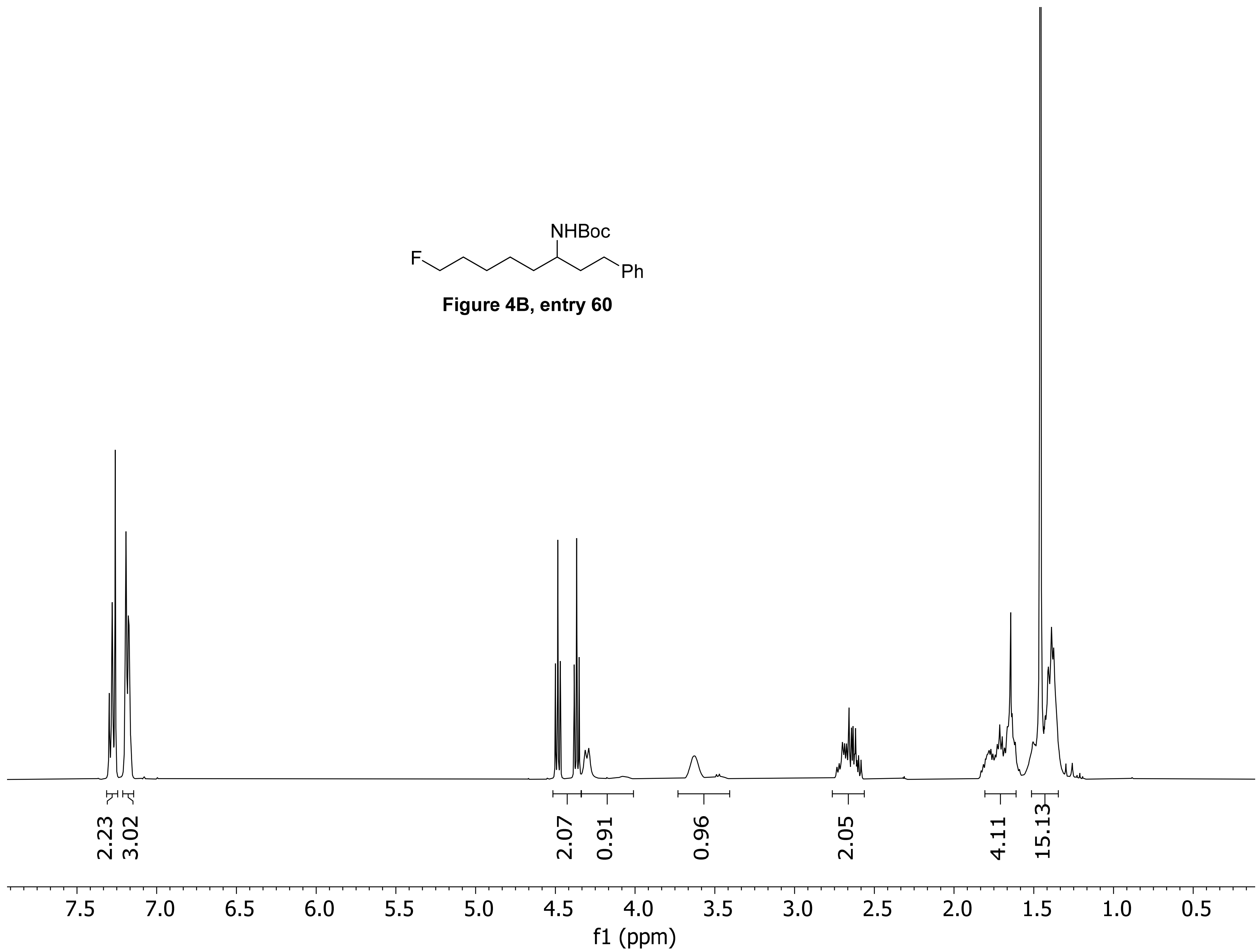
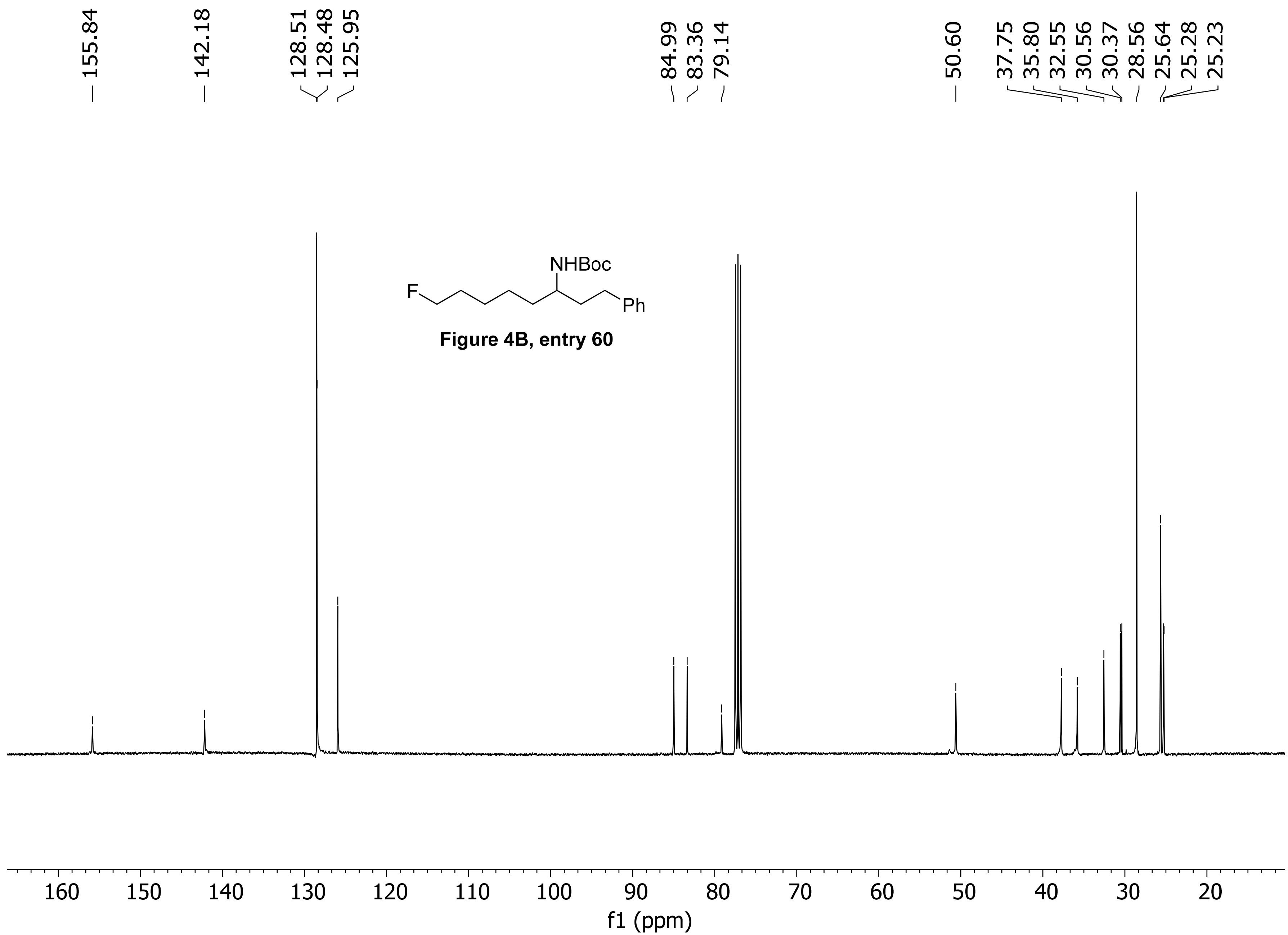
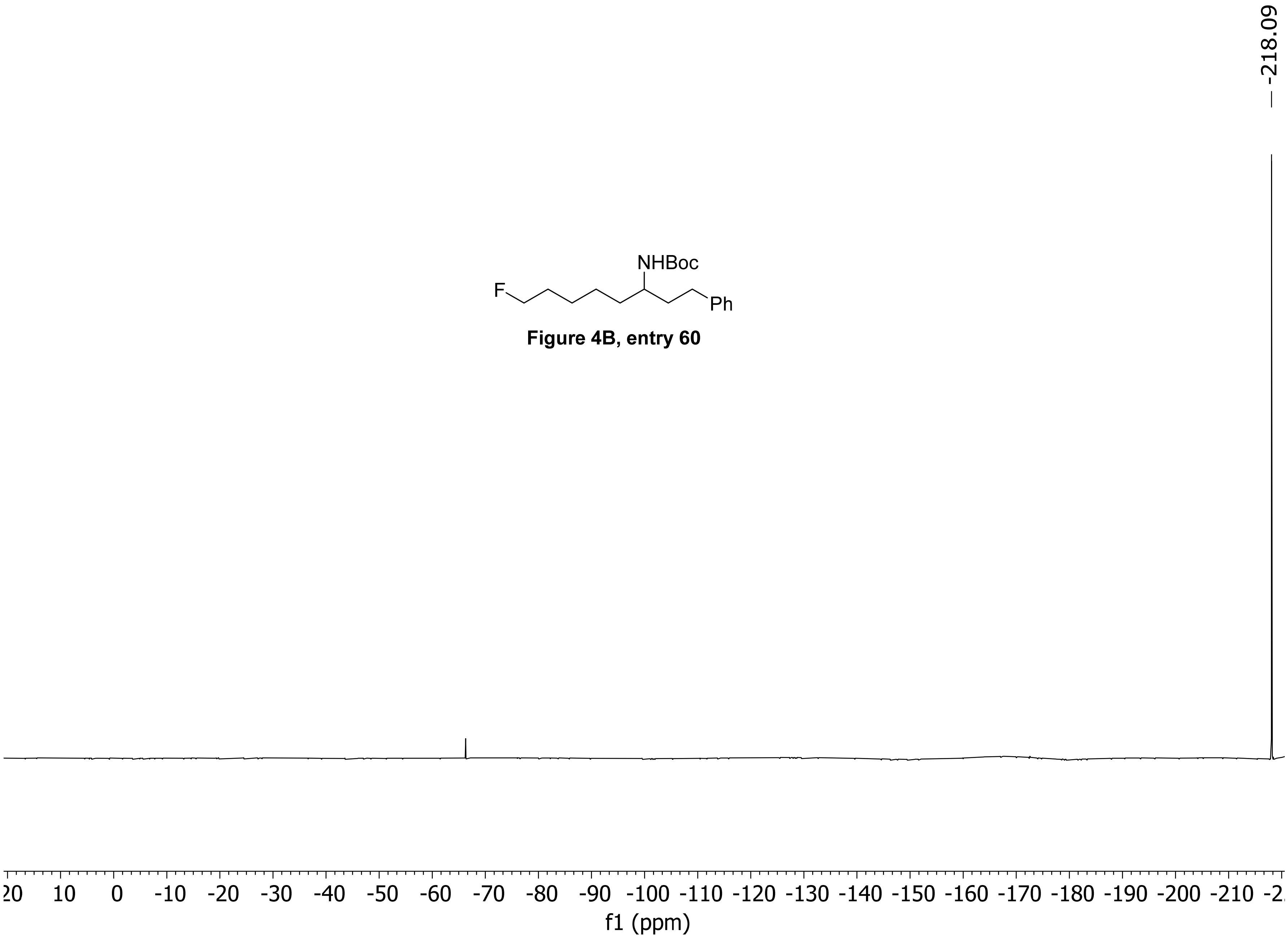
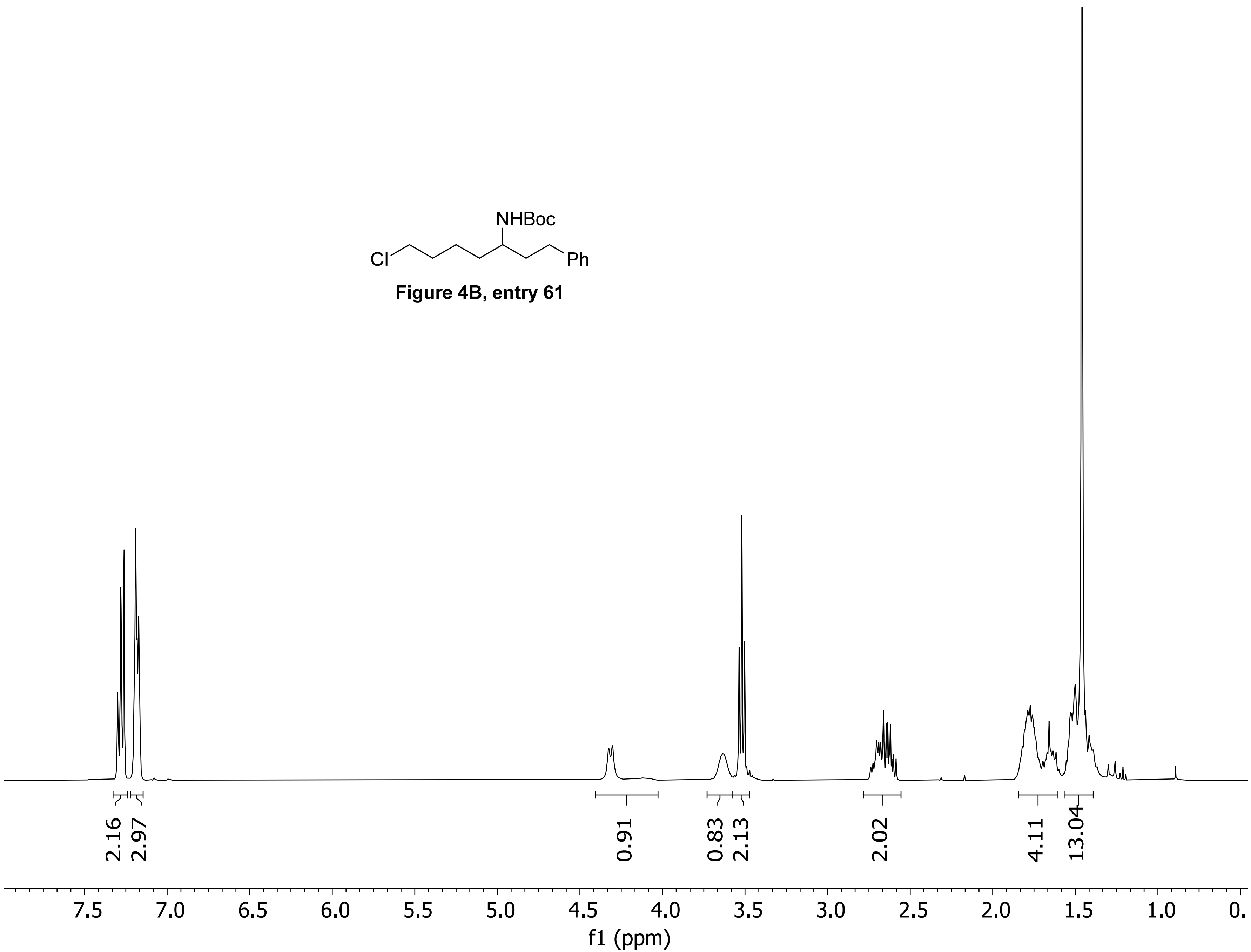


Figure 4B, entry 59


NHBoc
F
Ph
Figure 4B, entry 60
2.23
3.02
2.07
0.91
0.96
2.05
4.11
15.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


155.84
142.18
128.51
128.48
125.95
84.99
83.36
79.14
50.60
37.75
35.80
32.55
30.56
30.37
28.56
25.64
25.28
25.23
NHBoc
F
Ph
Figure 4B, entry 60
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


-218.09
NHBoc
F
Ph
Figure 4B, entry 60
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)


NHBoc
Cl
Ph
Figure 4B, entry 61
2.16
2.97
0.91
0.83
2.13
2.02
4.11
13.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
f1 (ppm)

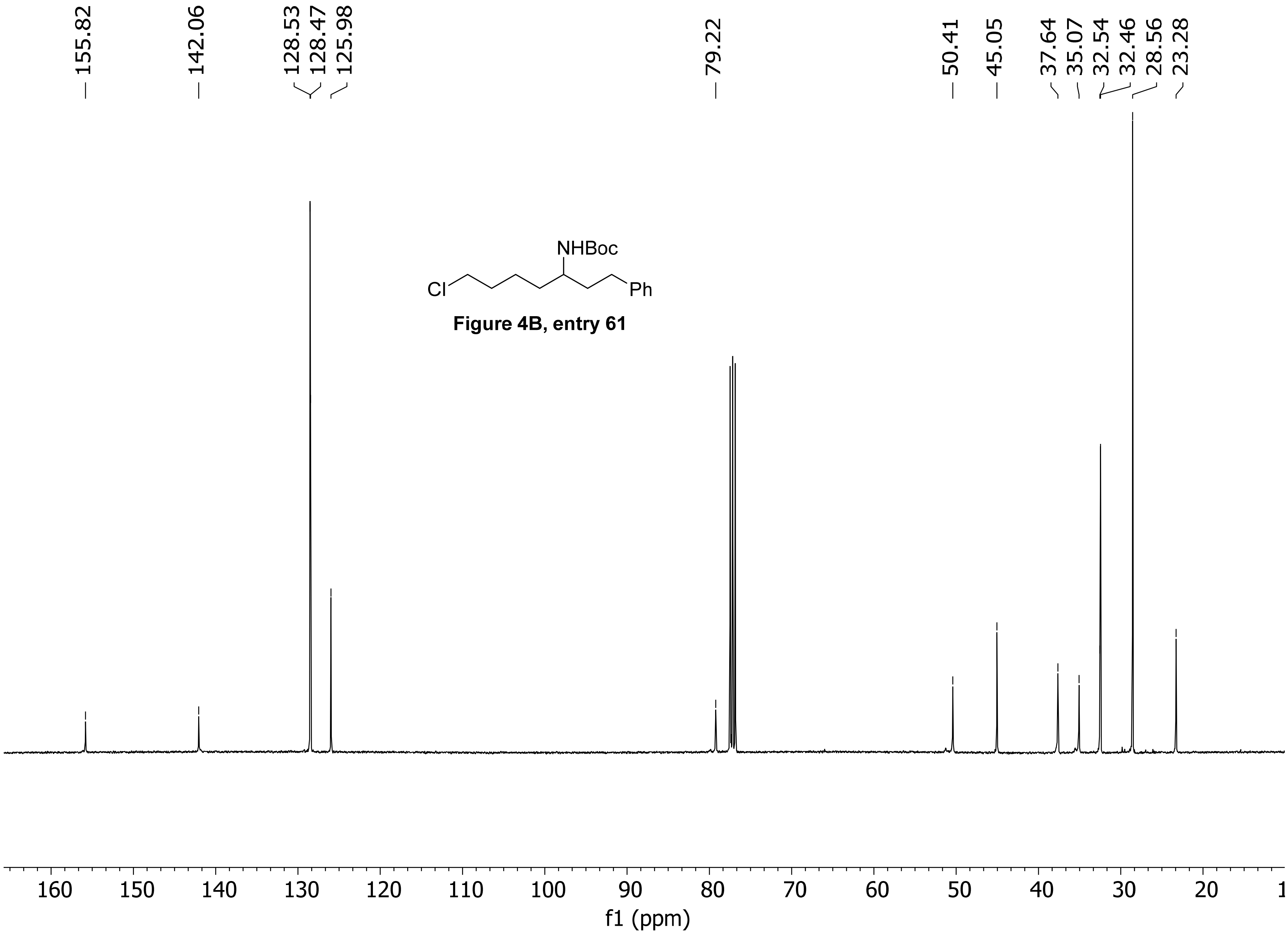


Figure 4B, entry 61

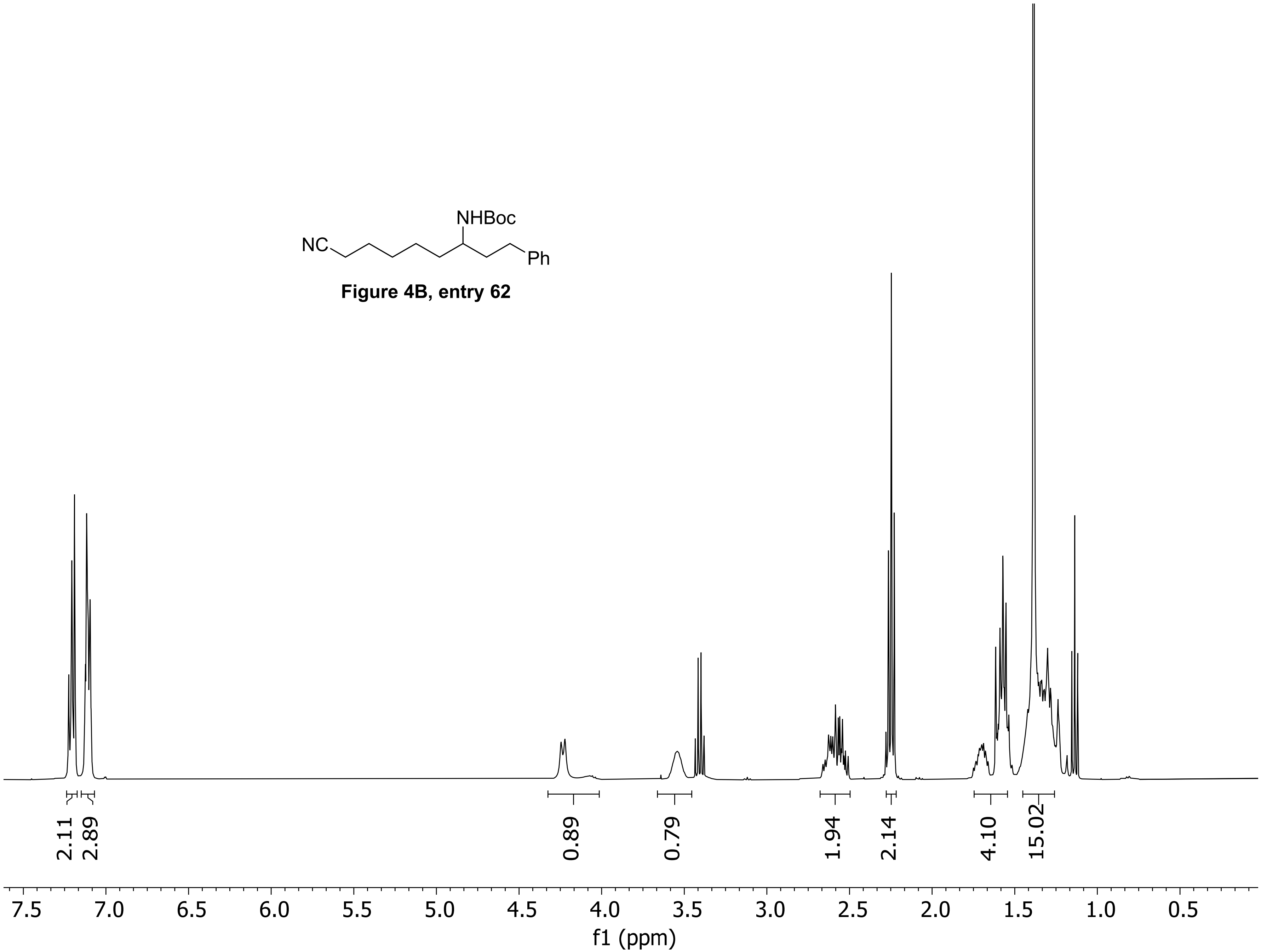


Figure 4B, entry 62

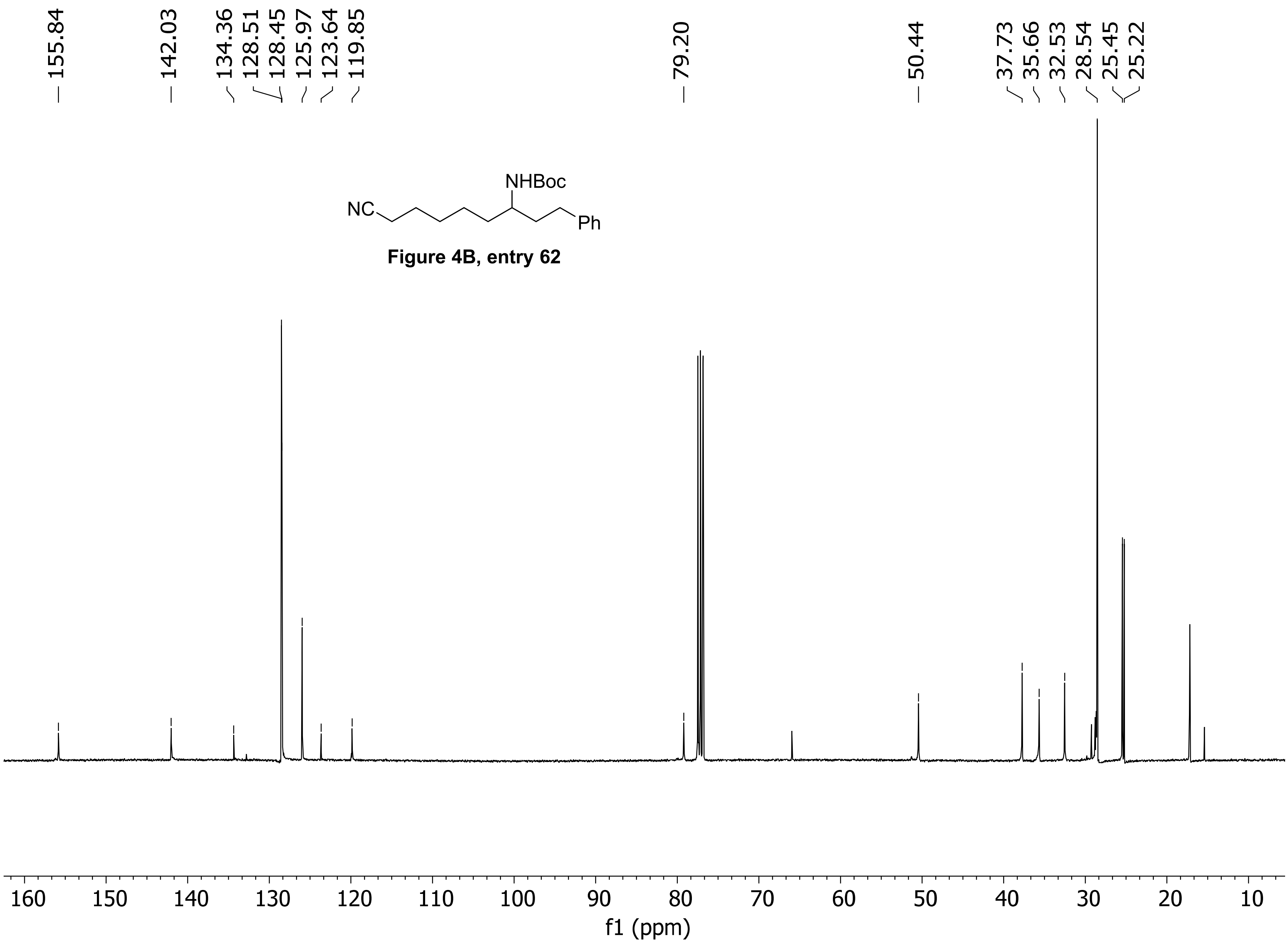


Figure 4B, entry 62

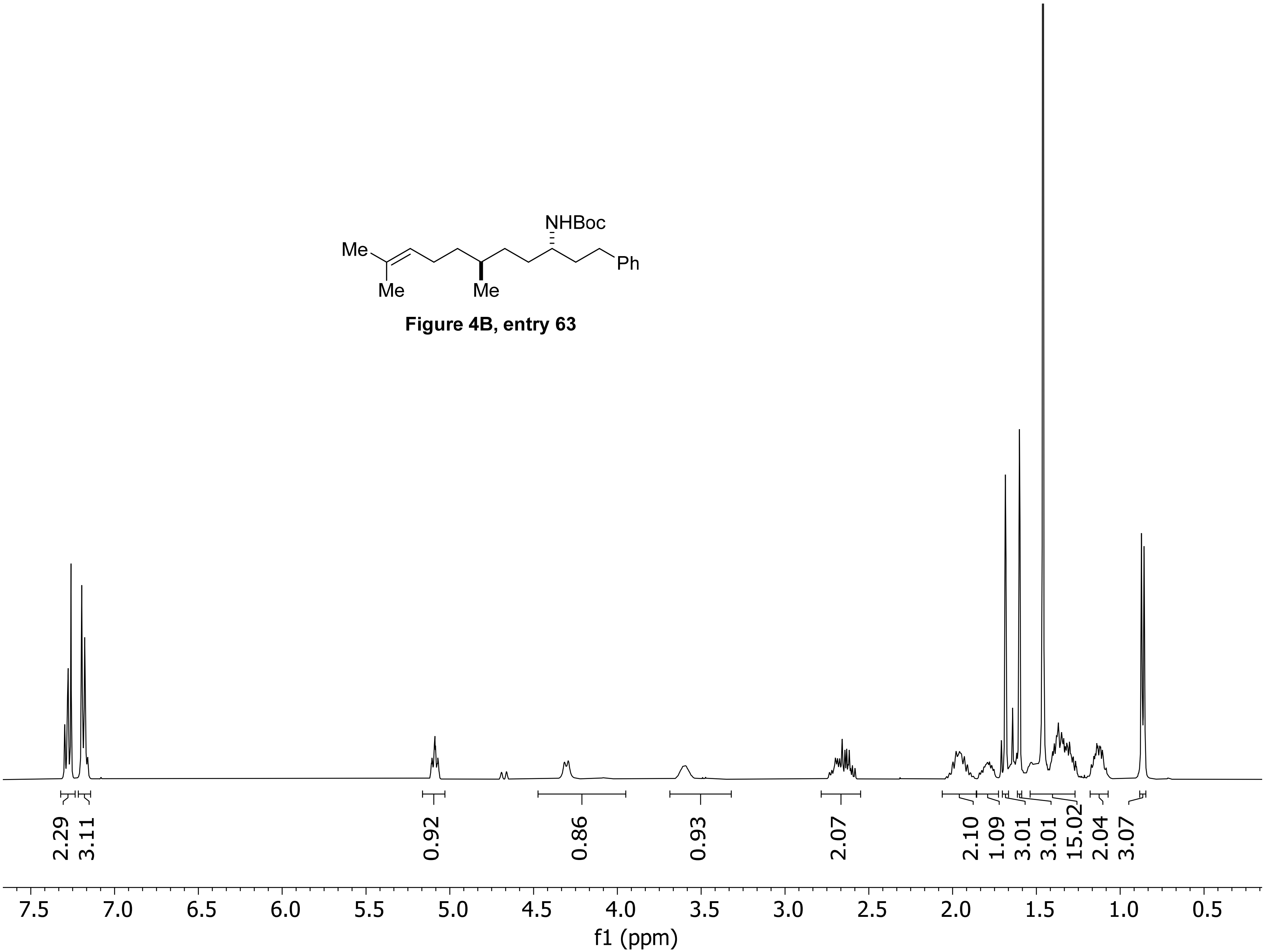
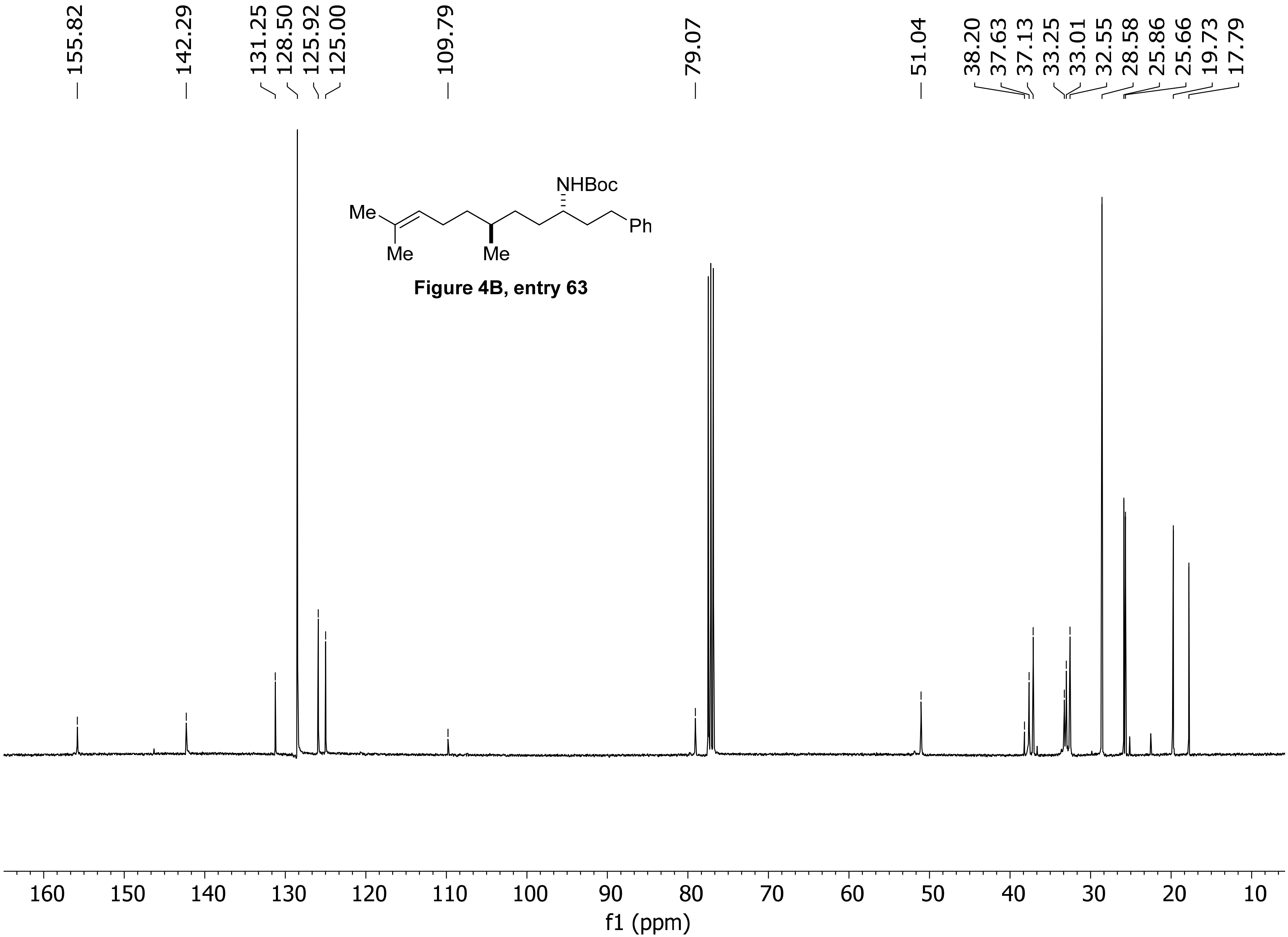


Figure 4B, entry 63


155.82
142.29
131.25
128.50
125.92
125.00
109.79
79.07
51.04
38.20
37.63
37.13
33.25
33.01
32.55
28.58
25.86
25.66
19.73
17.79
NHBoc
Me
Me
Me
Ph
Figure 4B, entry 63
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

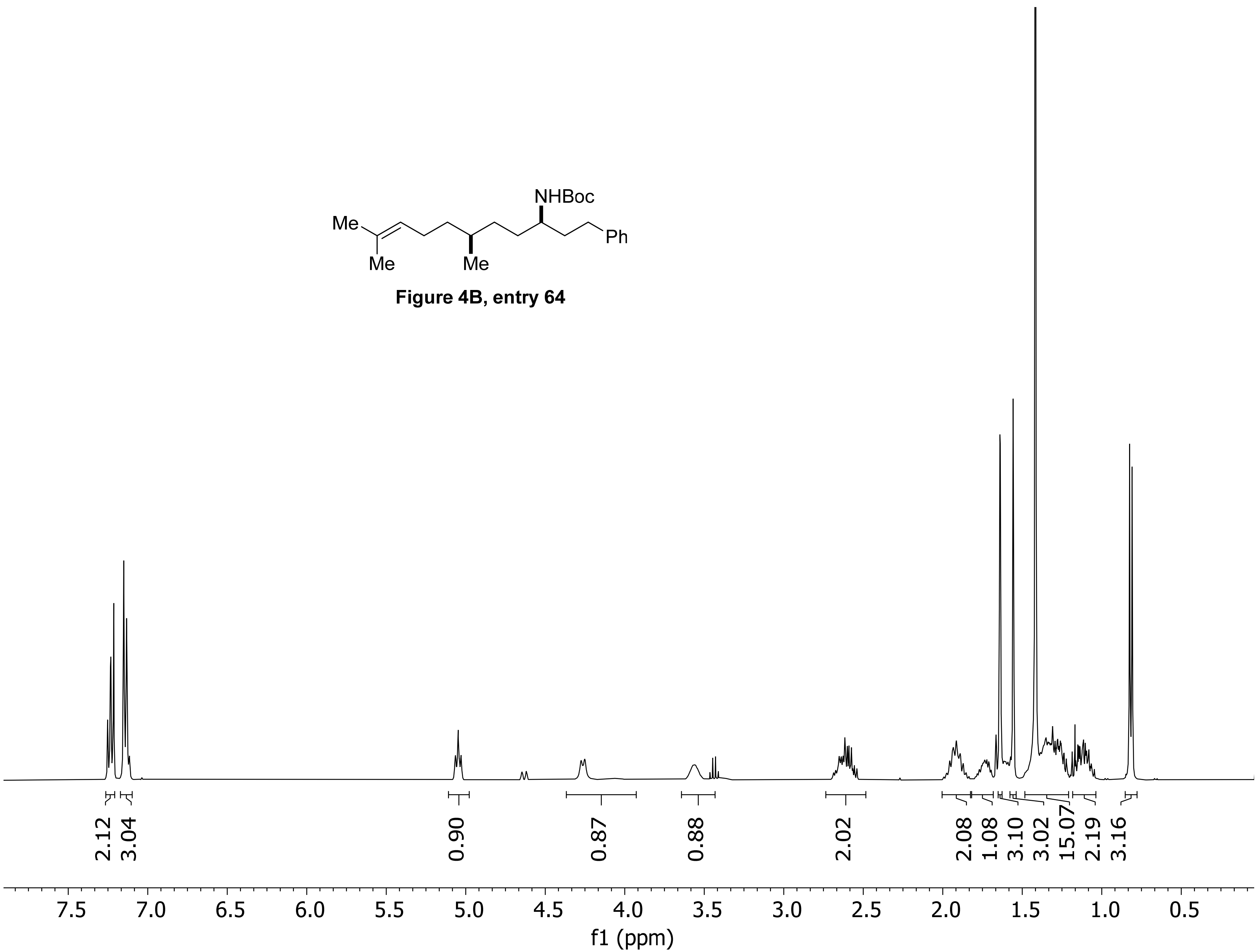


Figure 4B, entry 64

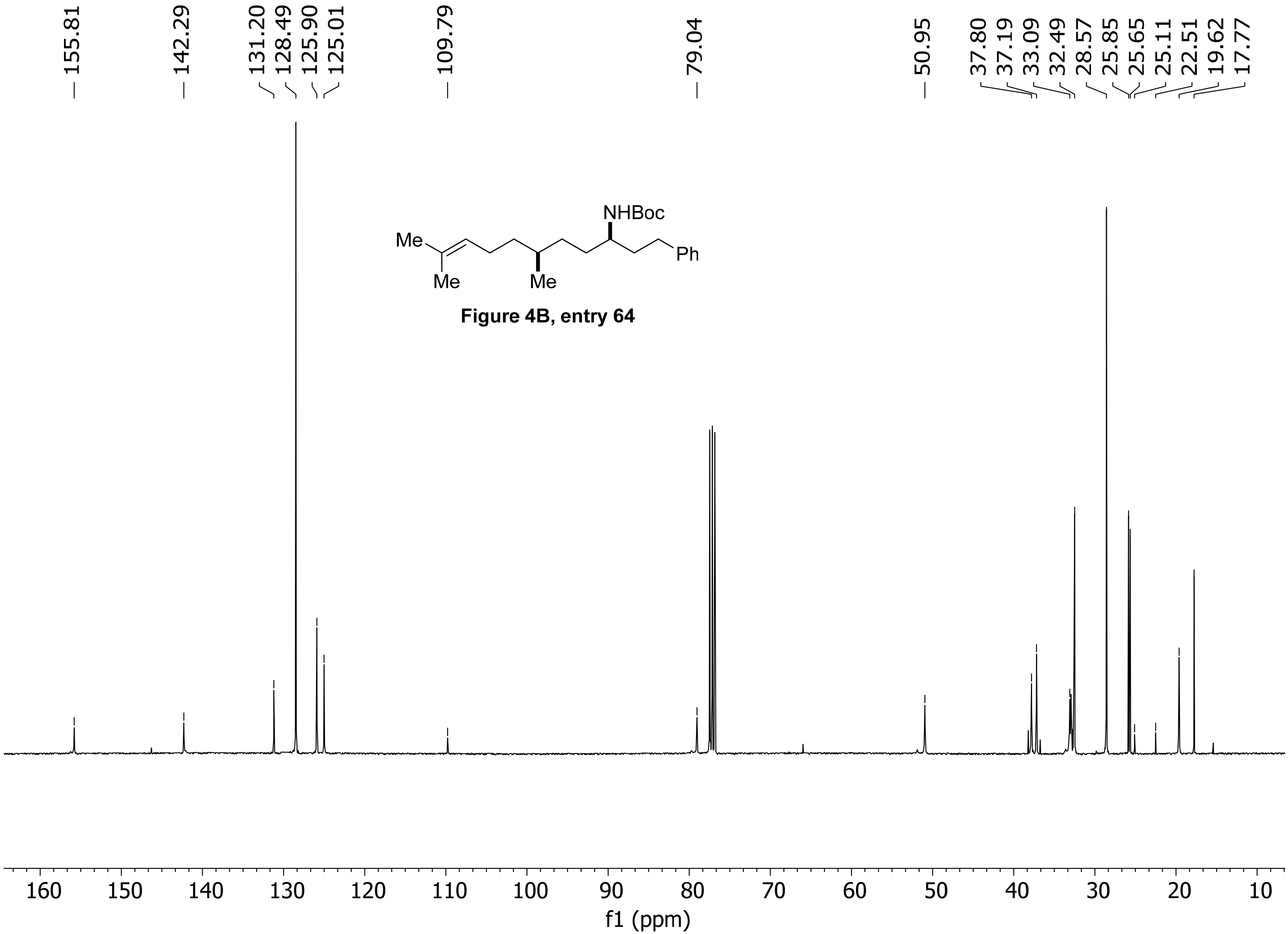


Figure 4B, entry 64

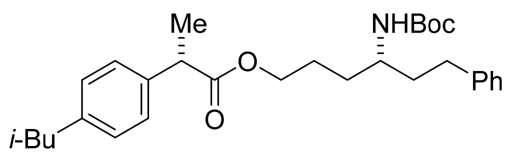
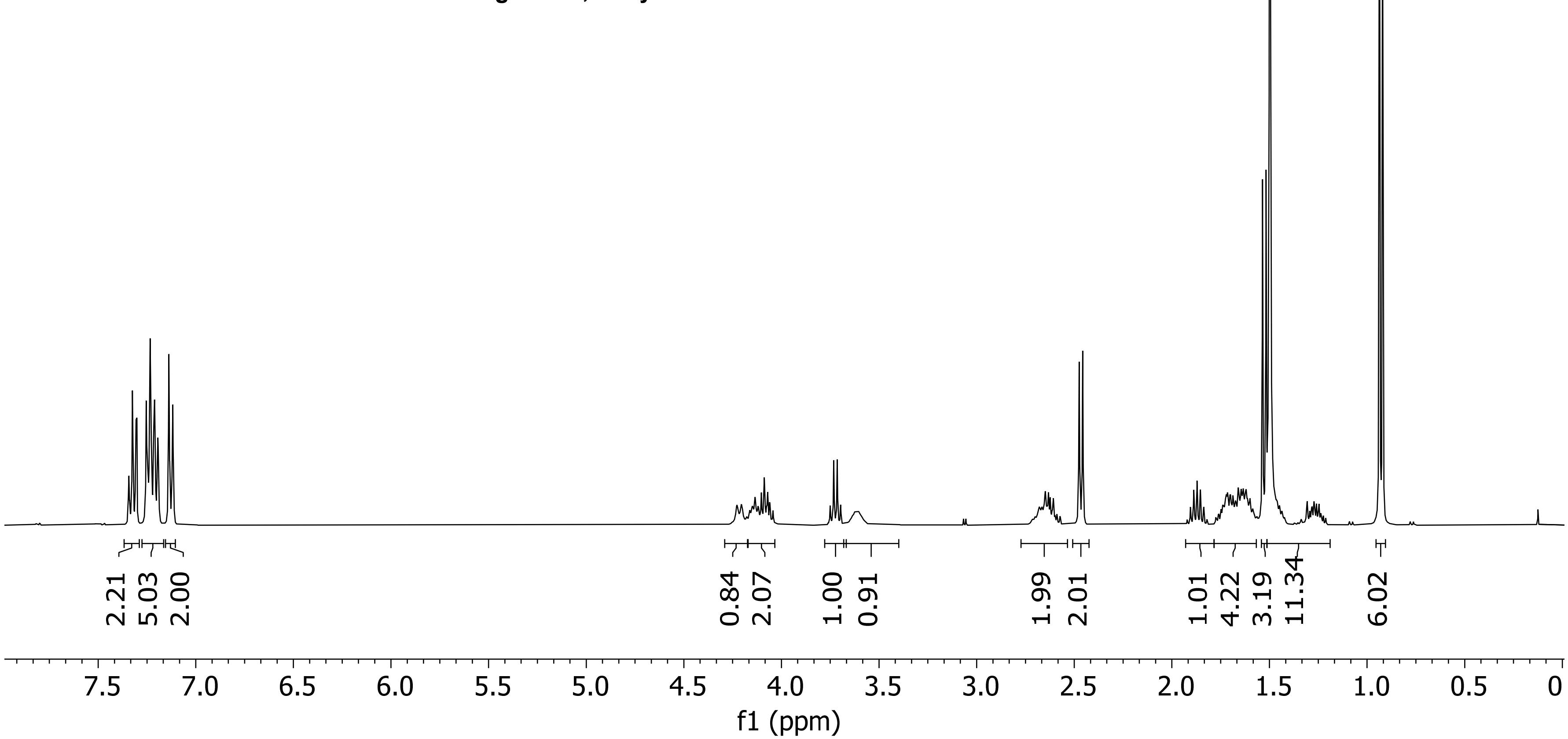


Figure 4B, entry 65



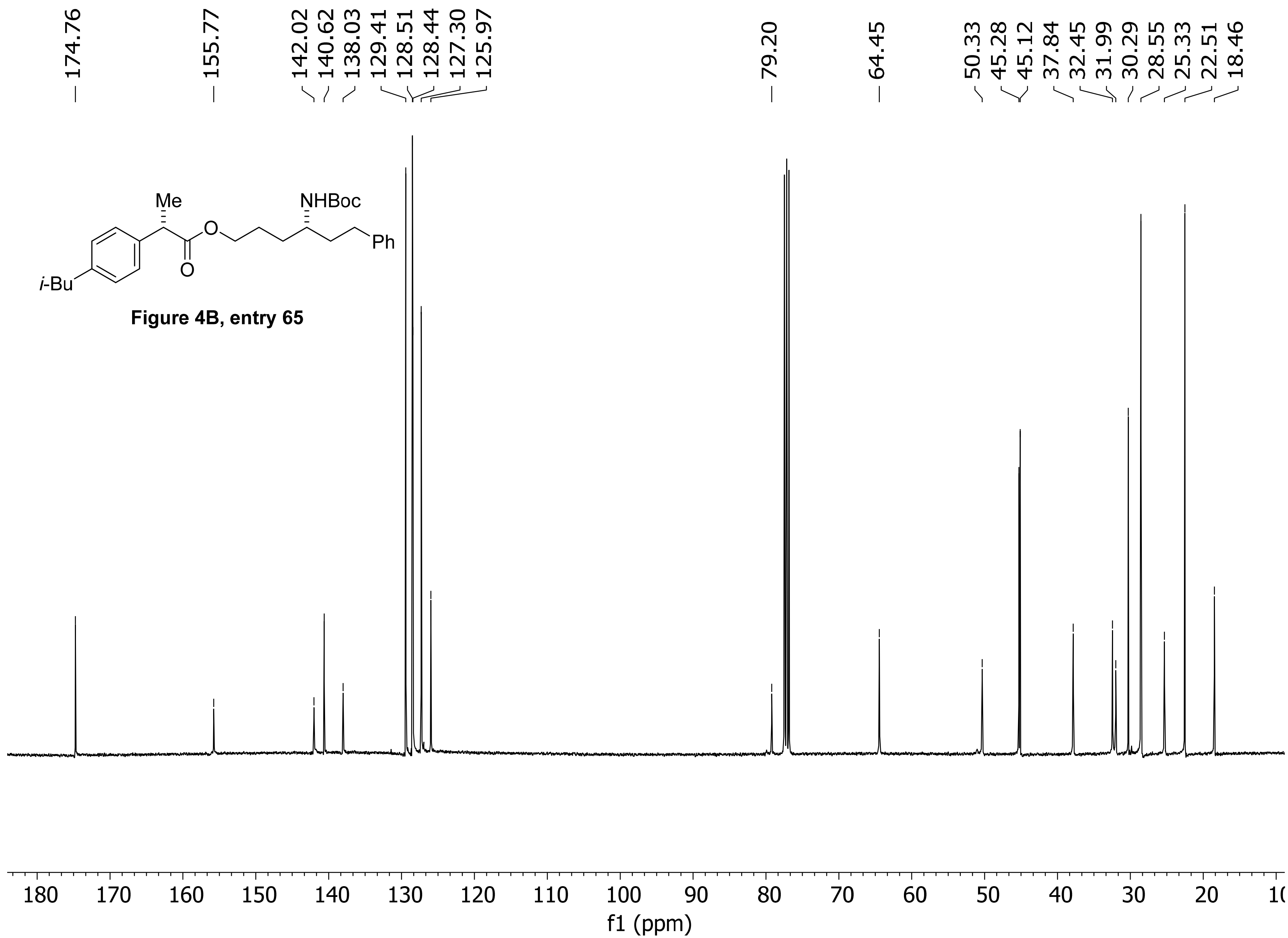


Figure 4B, entry 65

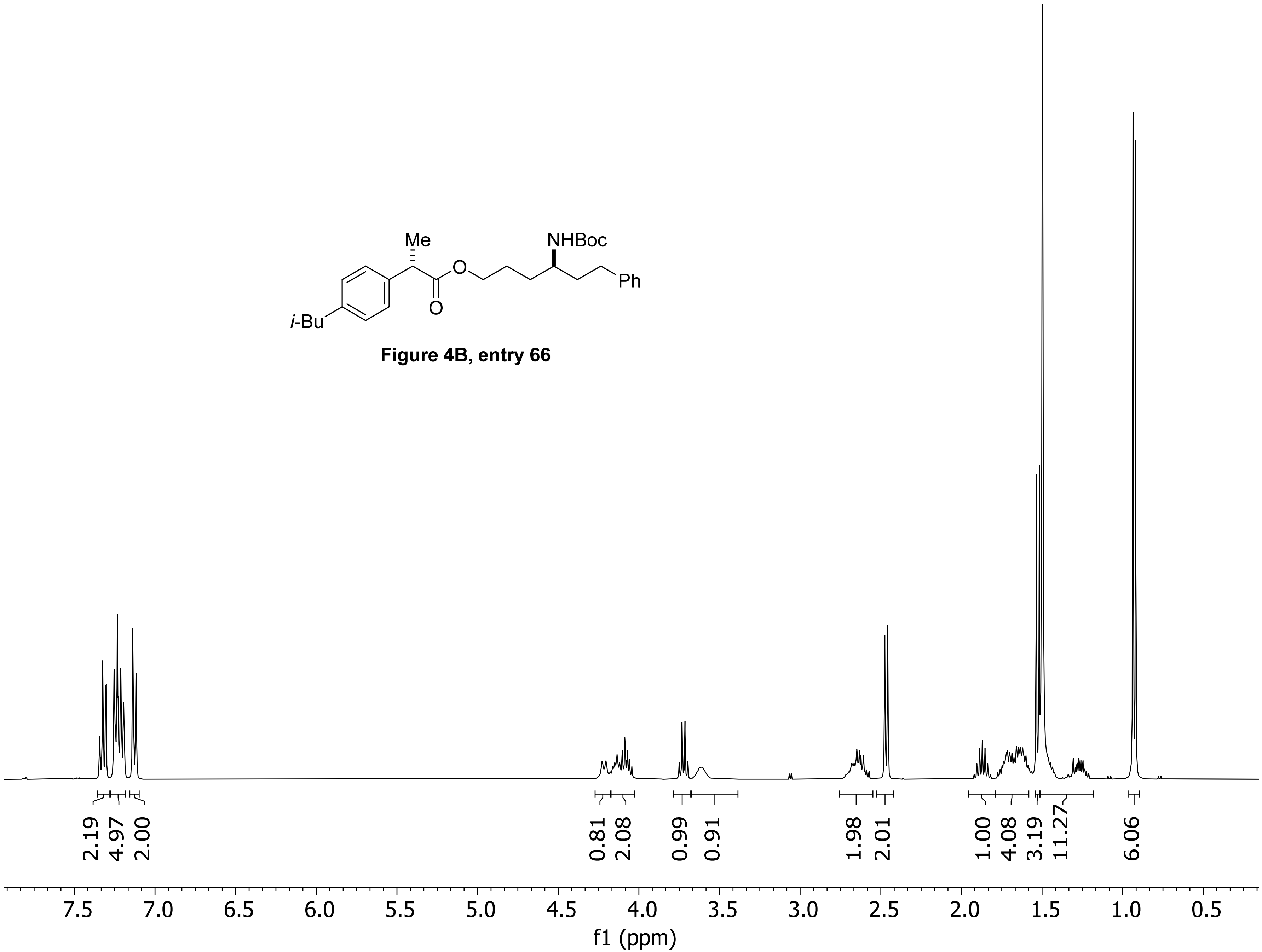
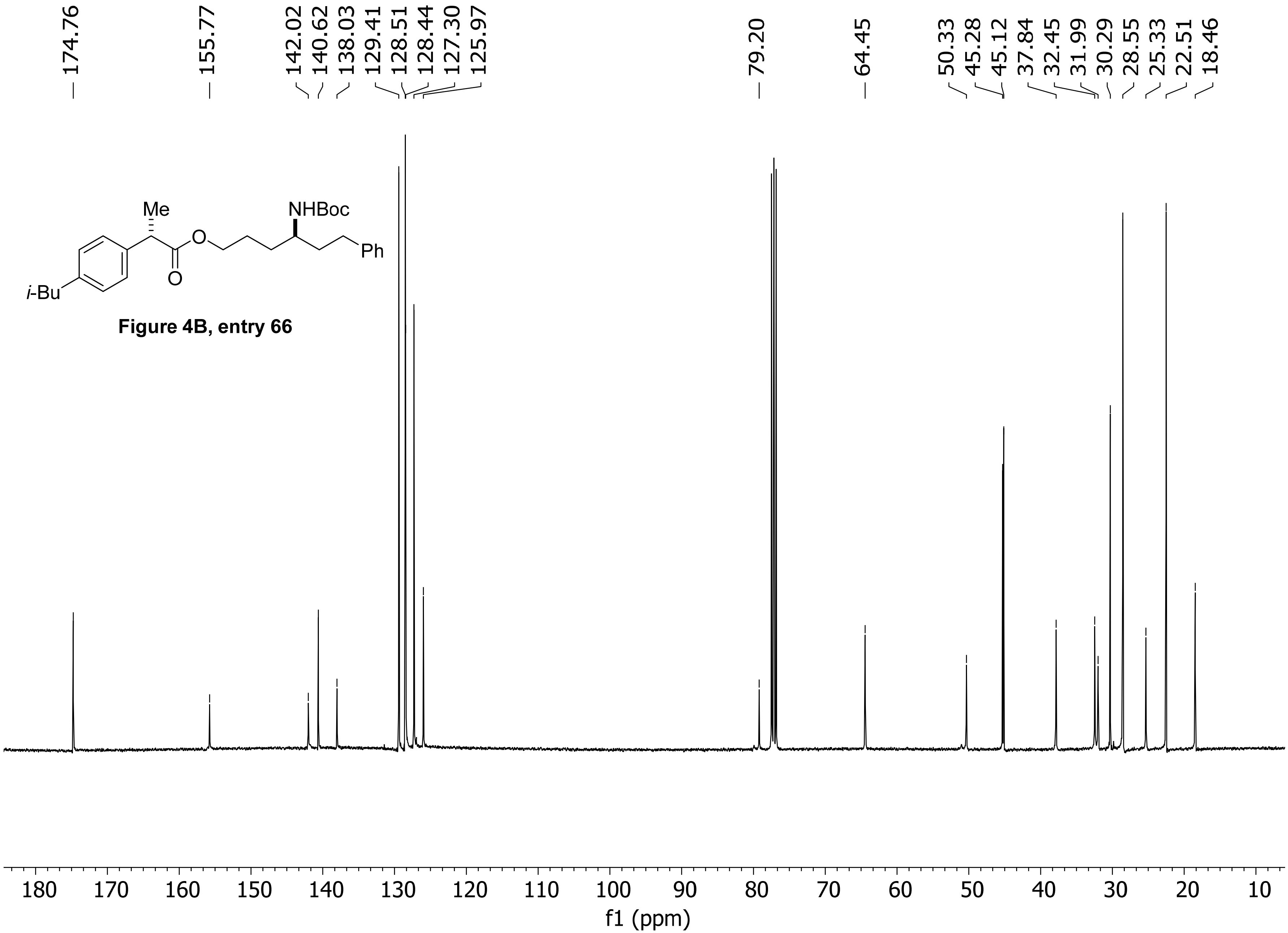


Figure 4B, entry 66


174.76
155.77
142.02
140.62
138.03
129.41
128.51
128.44
127.30
125.97
79.20
64.45
50.33
45.28
45.12
37.84
32.45
31.99
30.29
28.55
25.33
22.51
18.46
Me
NHBoc
O
Ph
O
i-Bu
Figure 4B, entry 66
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

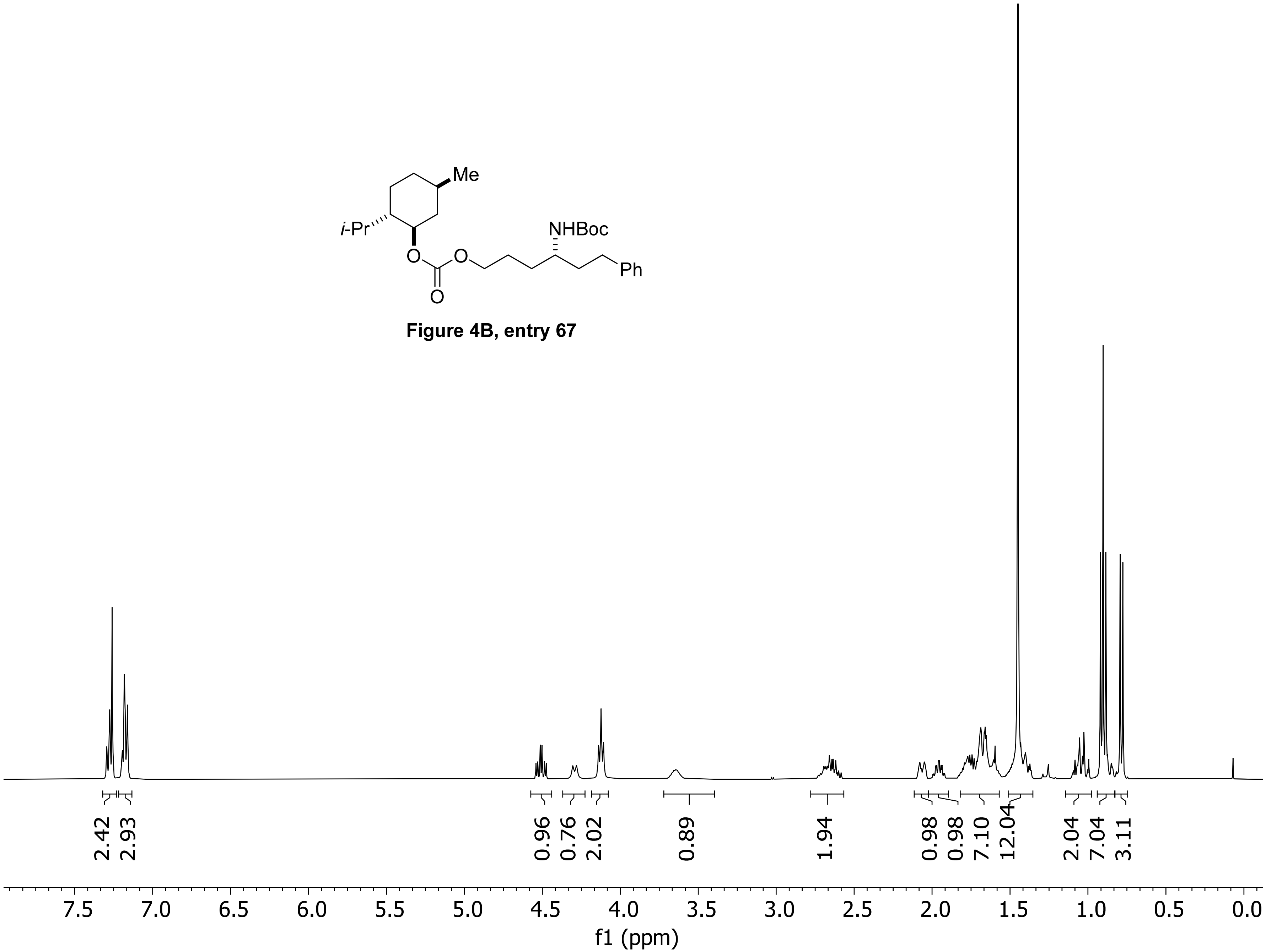


Figure 4B, entry 67

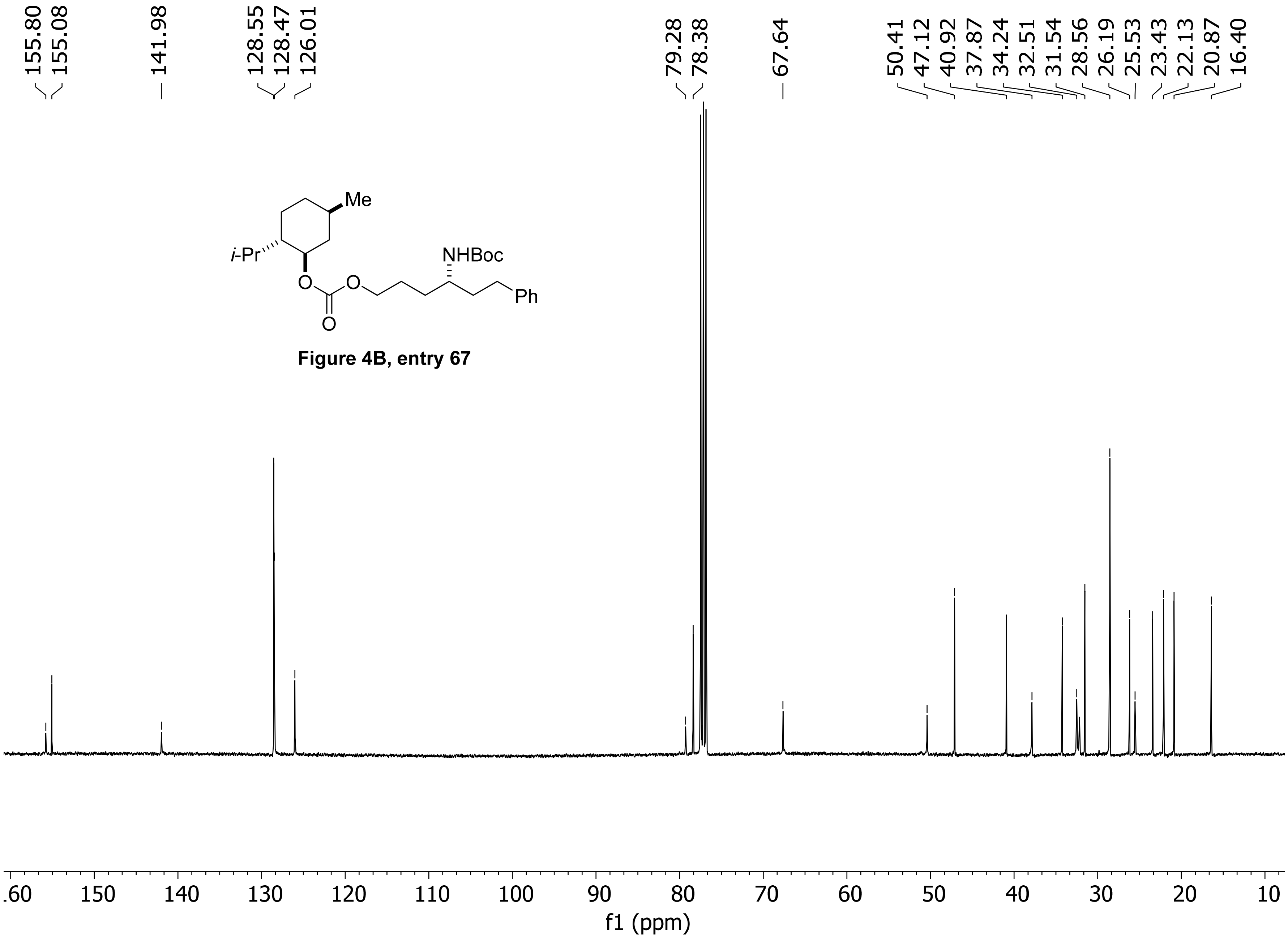


Figure 4B, entry 67

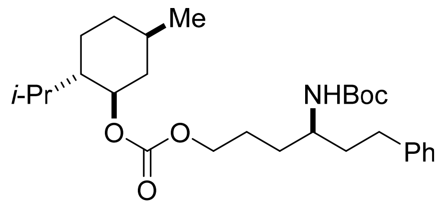
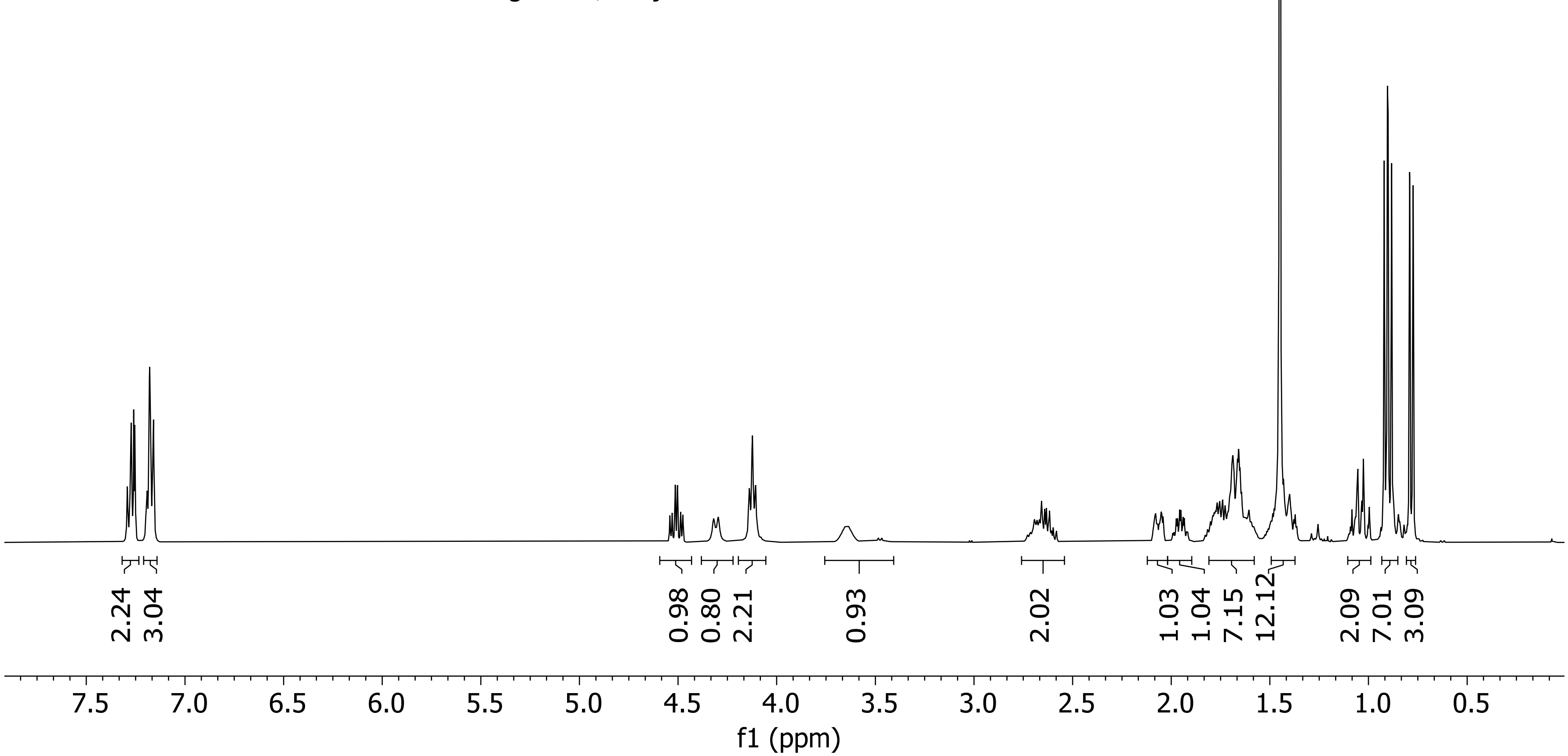
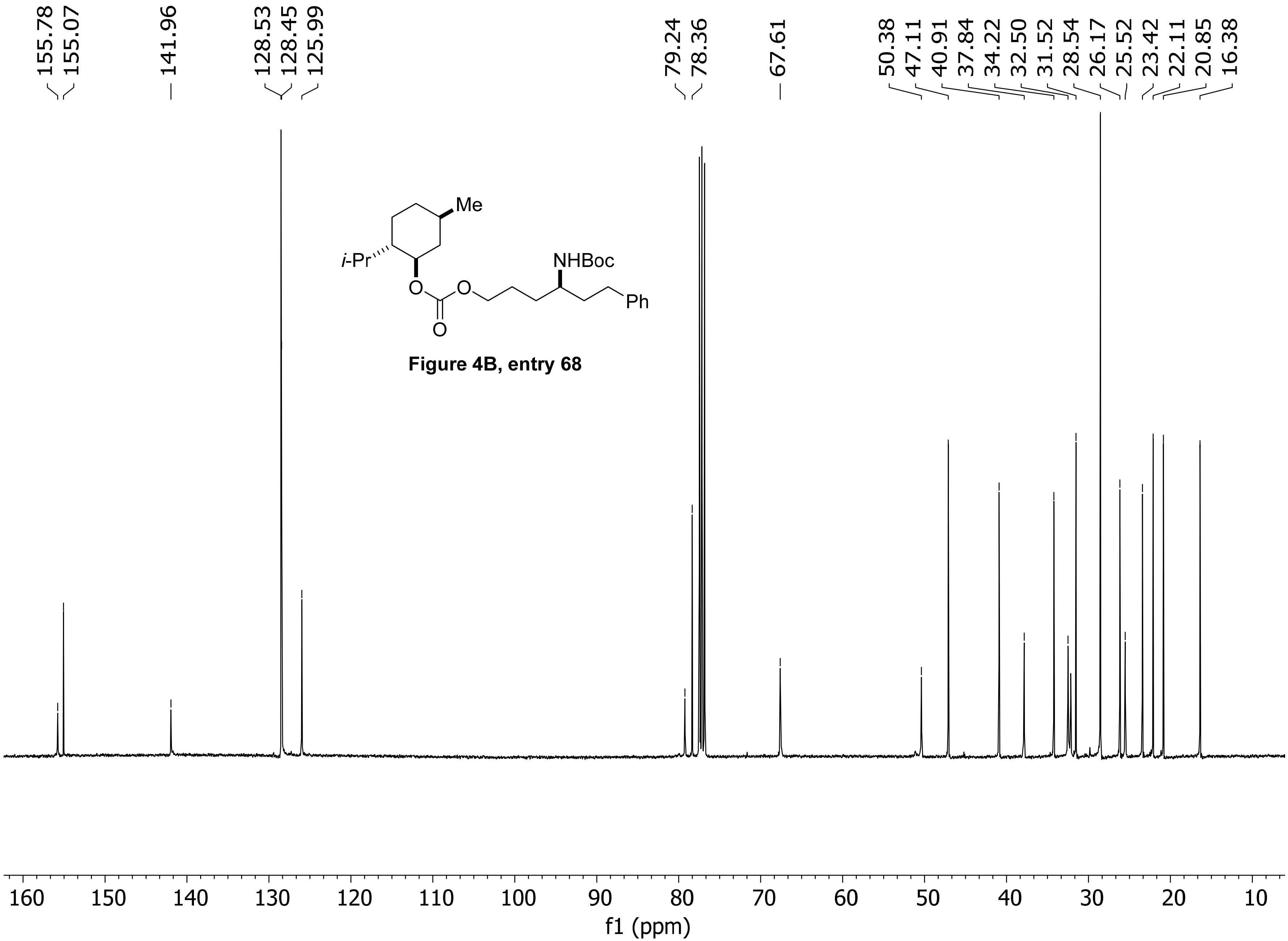


Figure 4B, entry 68




155.78
155.07
141.96
128.53
128.45
125.99
79.24
78.36
67.61
50.38
47.11
40.91
37.84
34.22
32.50
31.52
28.54
26.17
25.52
23.42
22.11
20.85
16.38
Me
i-Pr
NHBoc
O
O
O
Ph
Figure 4B, entry 68
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

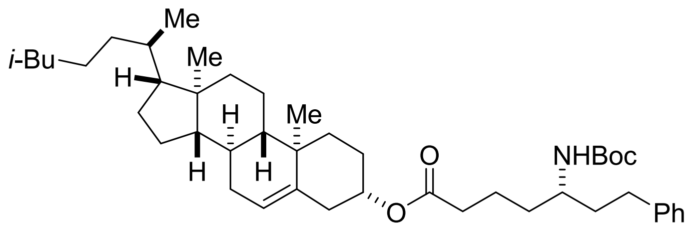
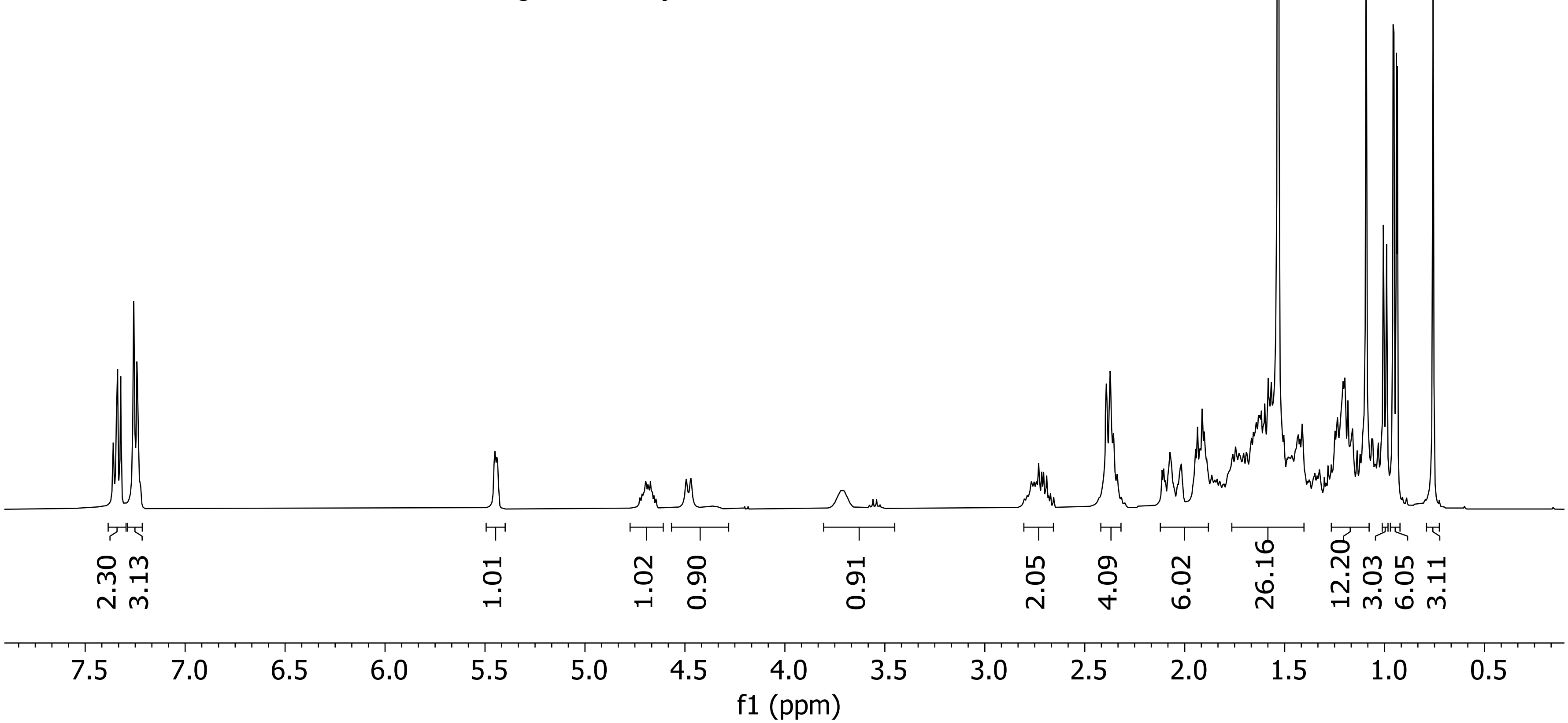


Figure 4B, entry 69



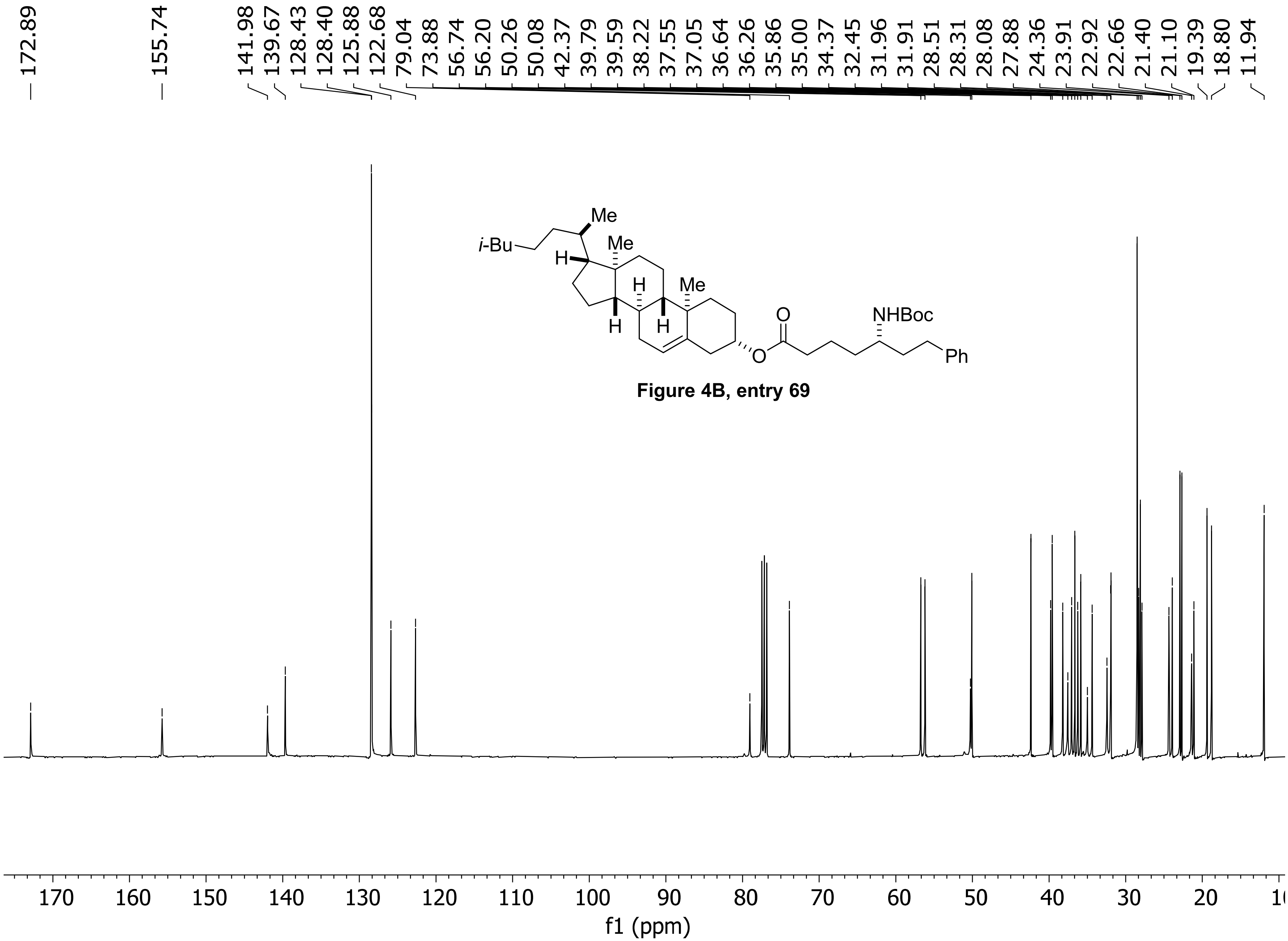


Figure 4B, entry 69

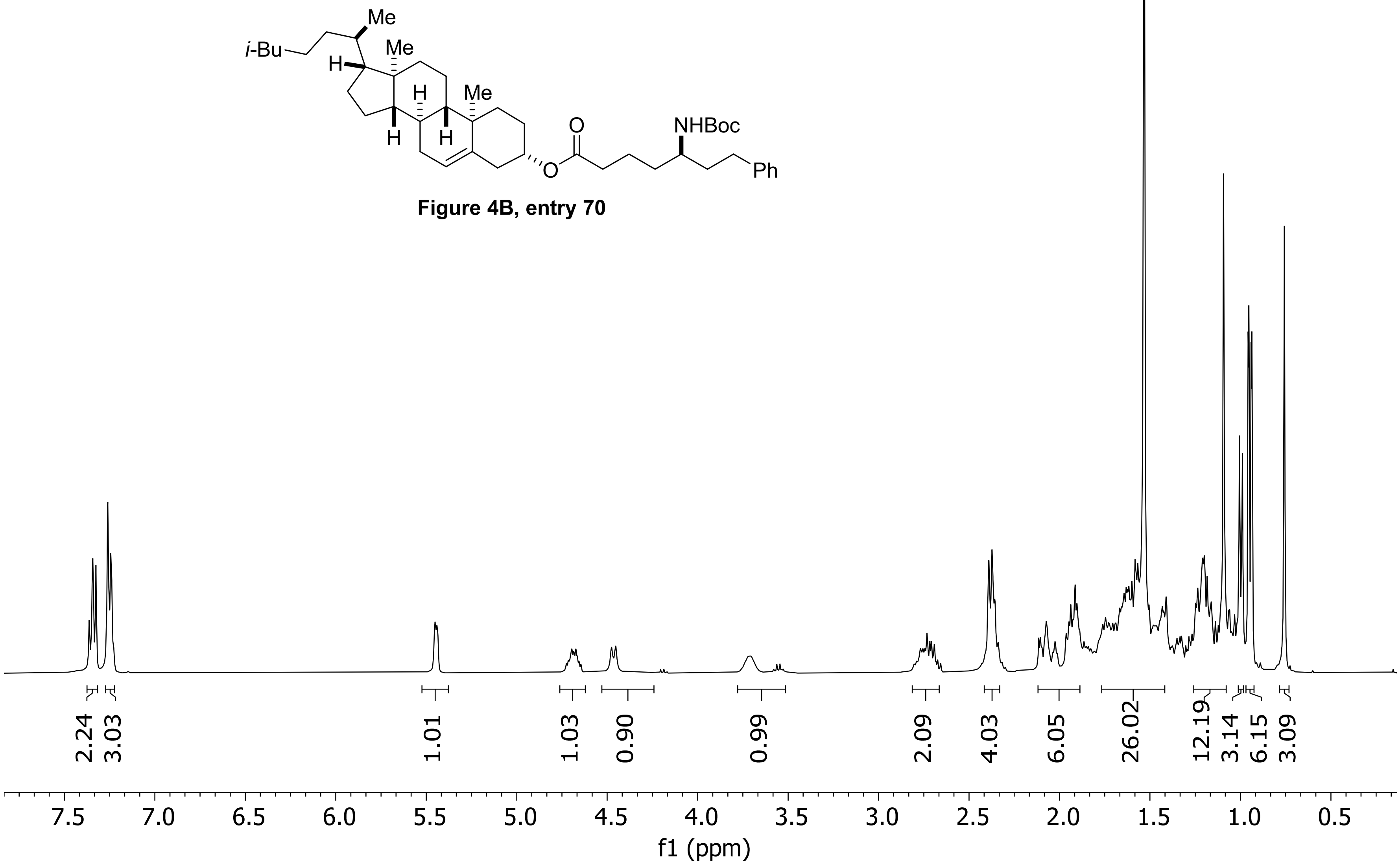
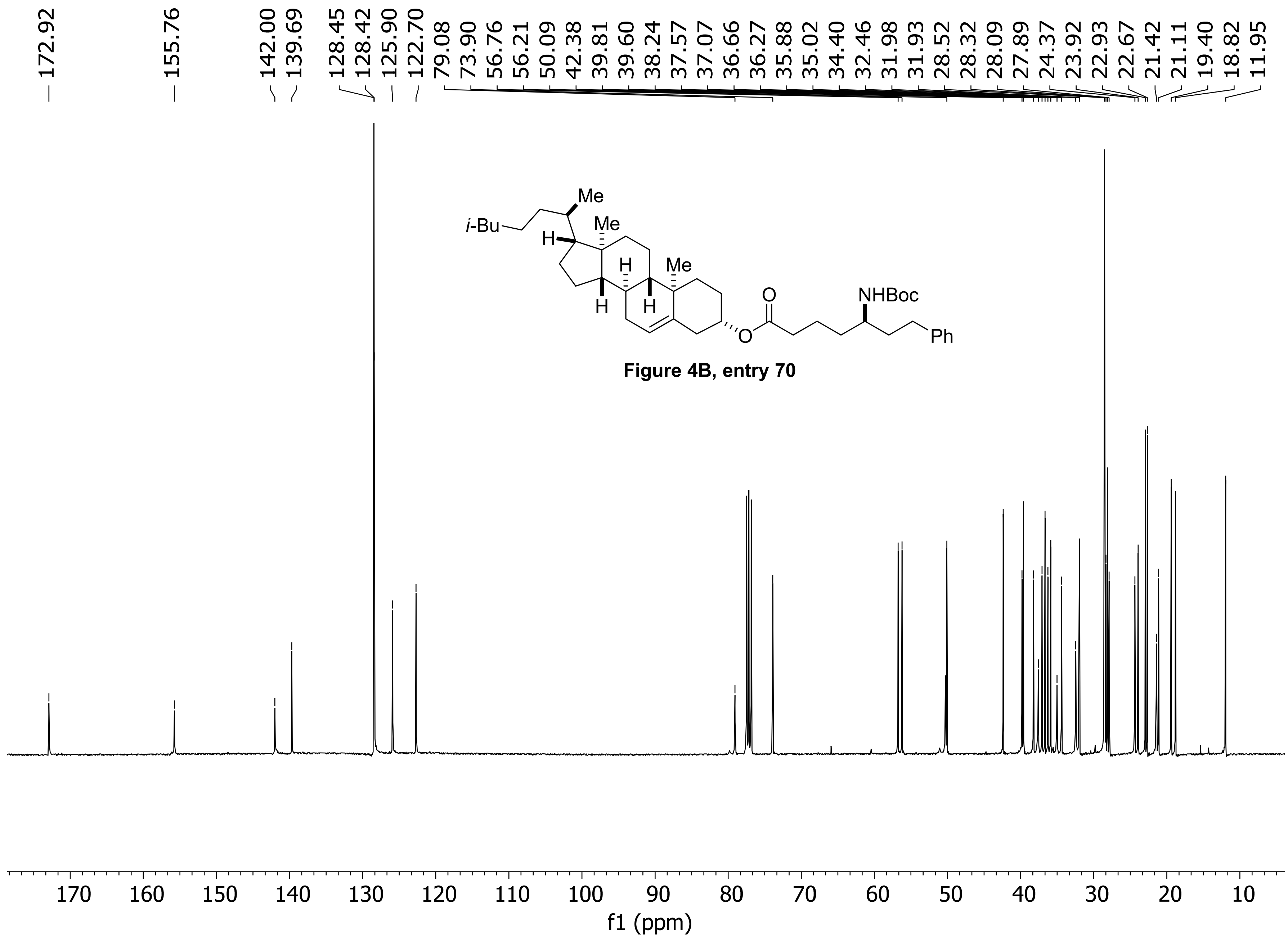


Figure 4B, entry 70


172.92
155.76
142.00
139.69
128.45
128.42
125.90
122.70
79.08
73.90
56.76
56.21
50.09
42.38
39.81
39.60
38.24
37.57
37.07
36.66
36.27
35.88
35.02
34.40
32.46
31.98
31.93
28.52
28.32
28.09
27.89
24.37
23.92
22.93
22.67
21.42
21.11
19.40
18.82
11.95
Me
i-Bu
Me
H
H
Me
H
H
O
NHBoc
O
Ph
Figure 4B, entry 70
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

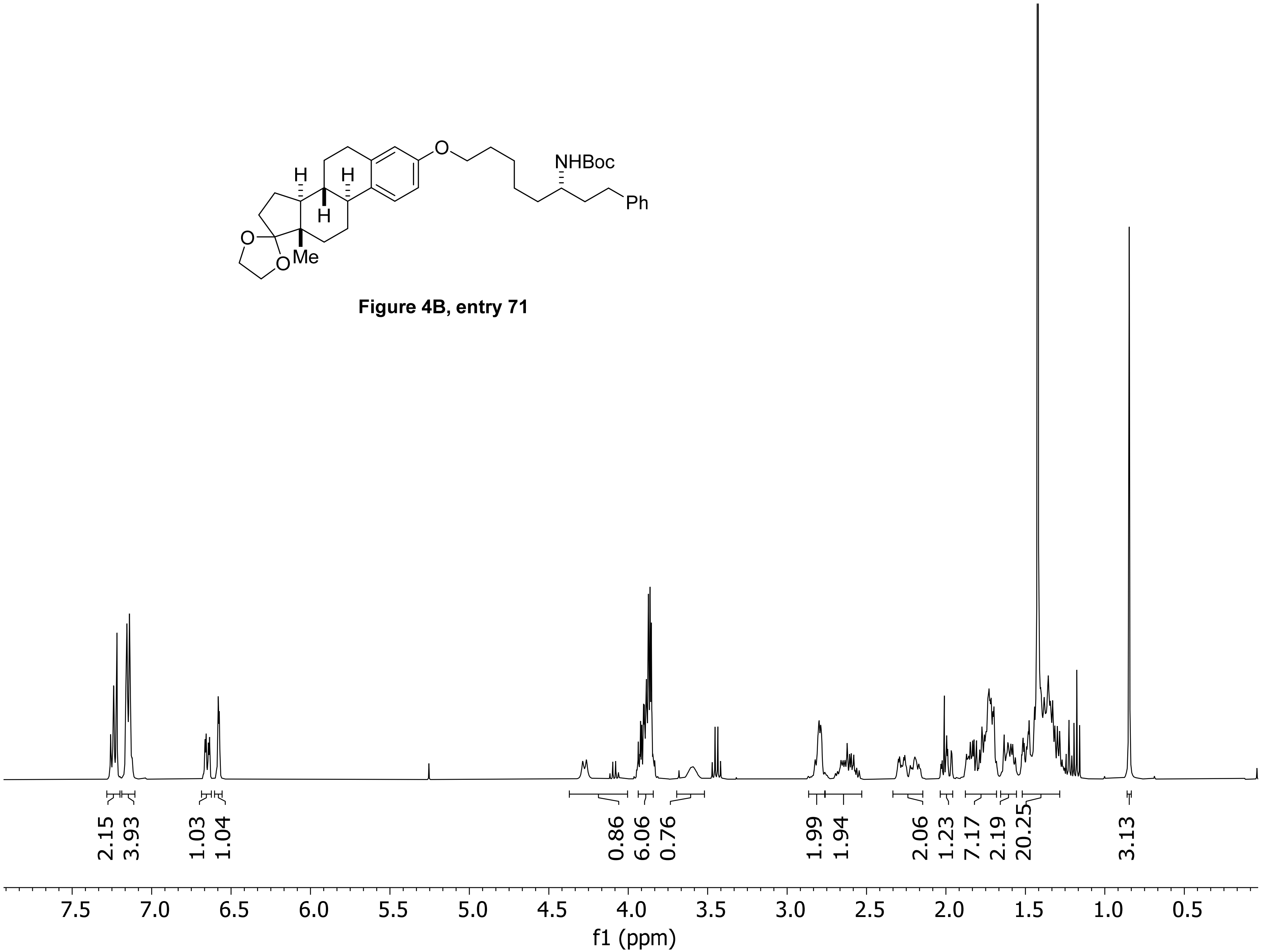
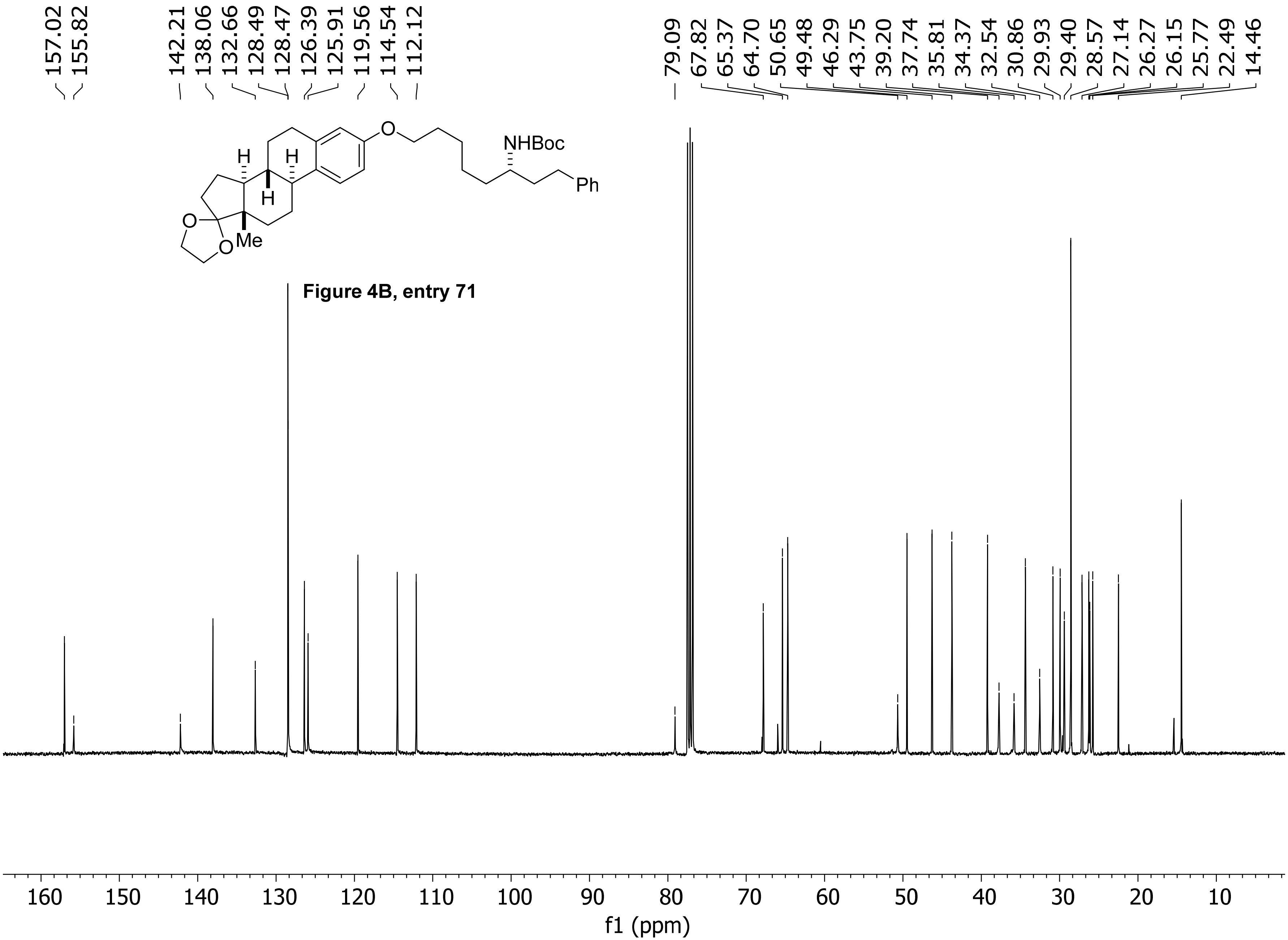


Figure 4B, entry 71


157.02
155.82
142.21
138.06
132.66
128.49
128.47
126.39
125.91
119.56
114.54
112.12
79.09
67.82
65.37
64.70
50.65
49.48
46.29
43.75
39.20
37.74
35.81
34.37
32.54
30.86
29.93
29.40
28.57
27.14
26.27
26.15
25.77
22.49
14.46
NHBoc
Ph
Me
Figure 4B, entry 71
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

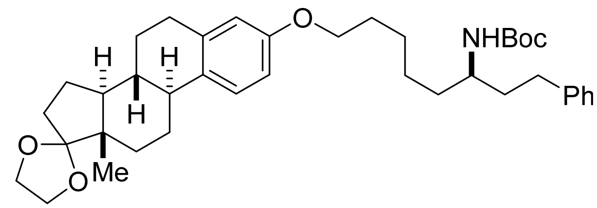
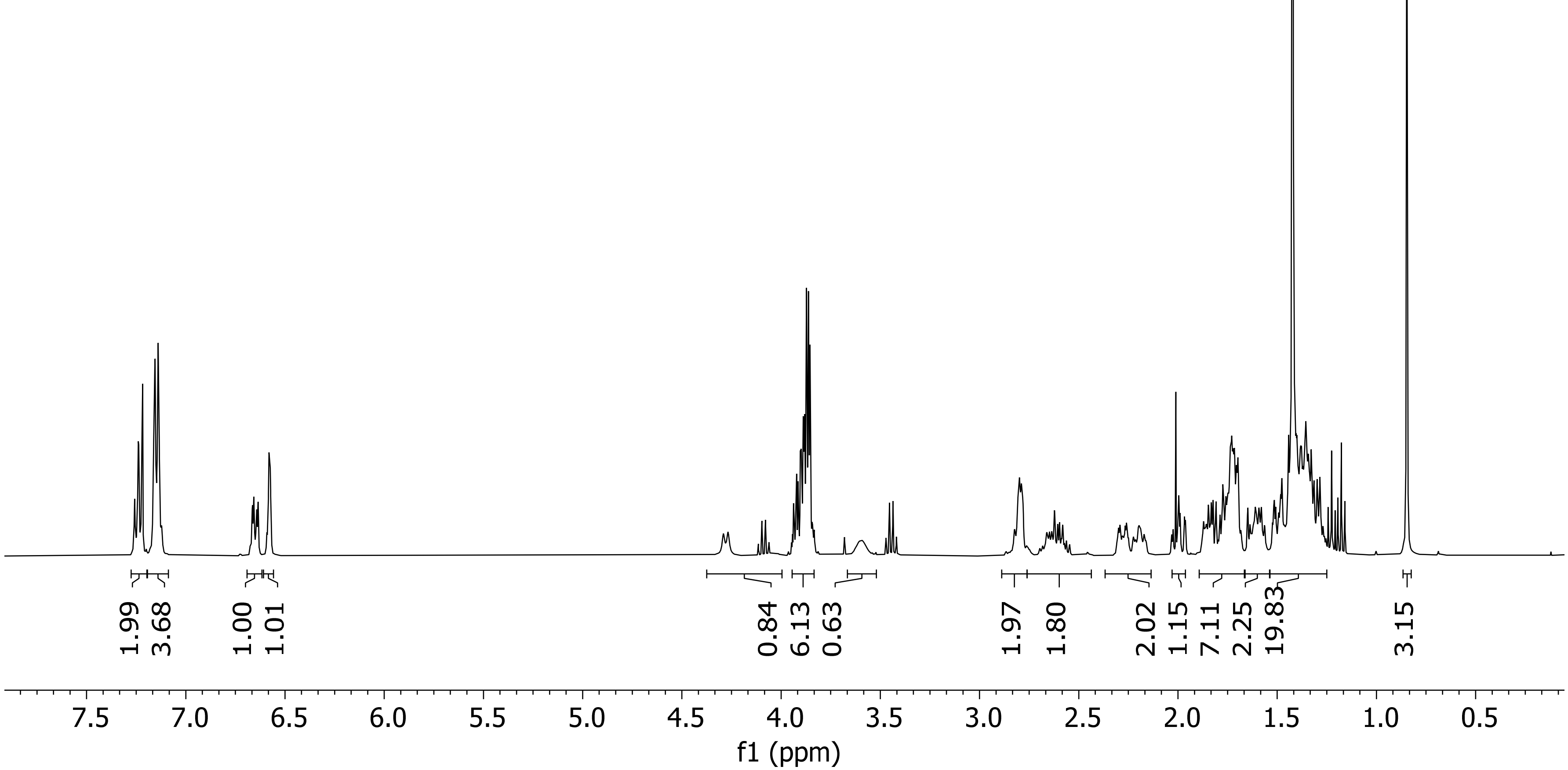


Figure 4B, entry 72



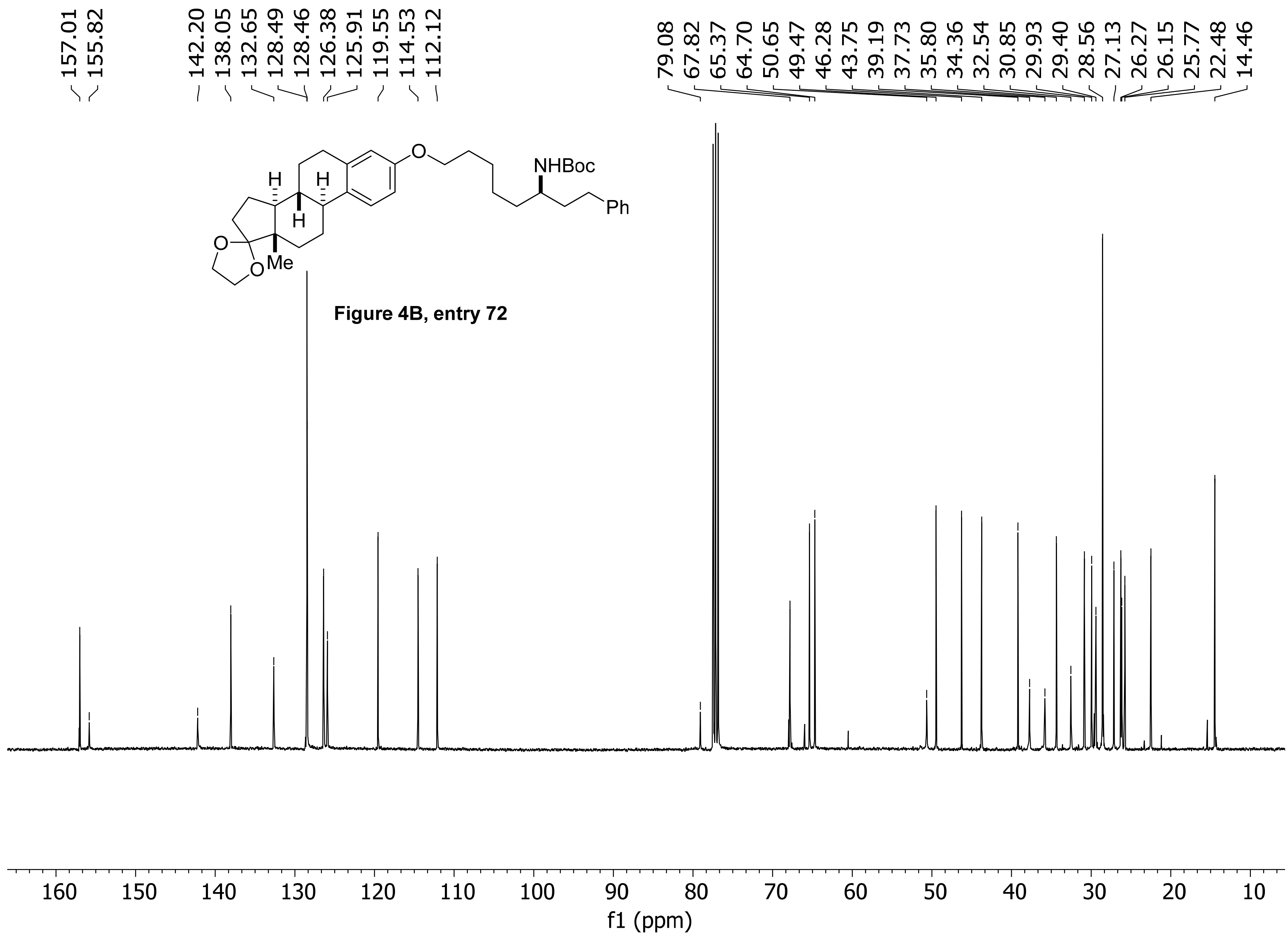


Figure 4B, entry 72

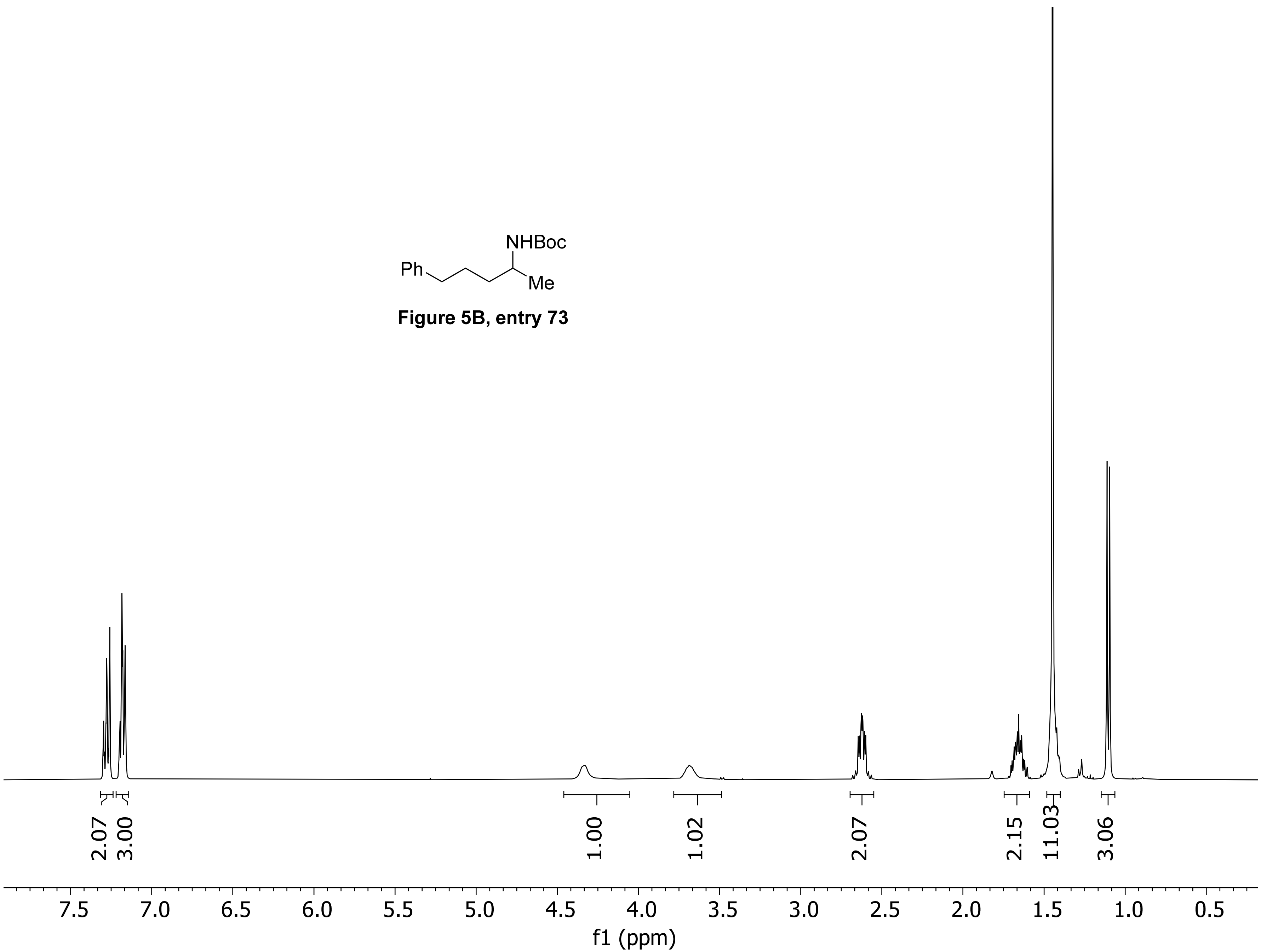


Figure 5B, entry 73

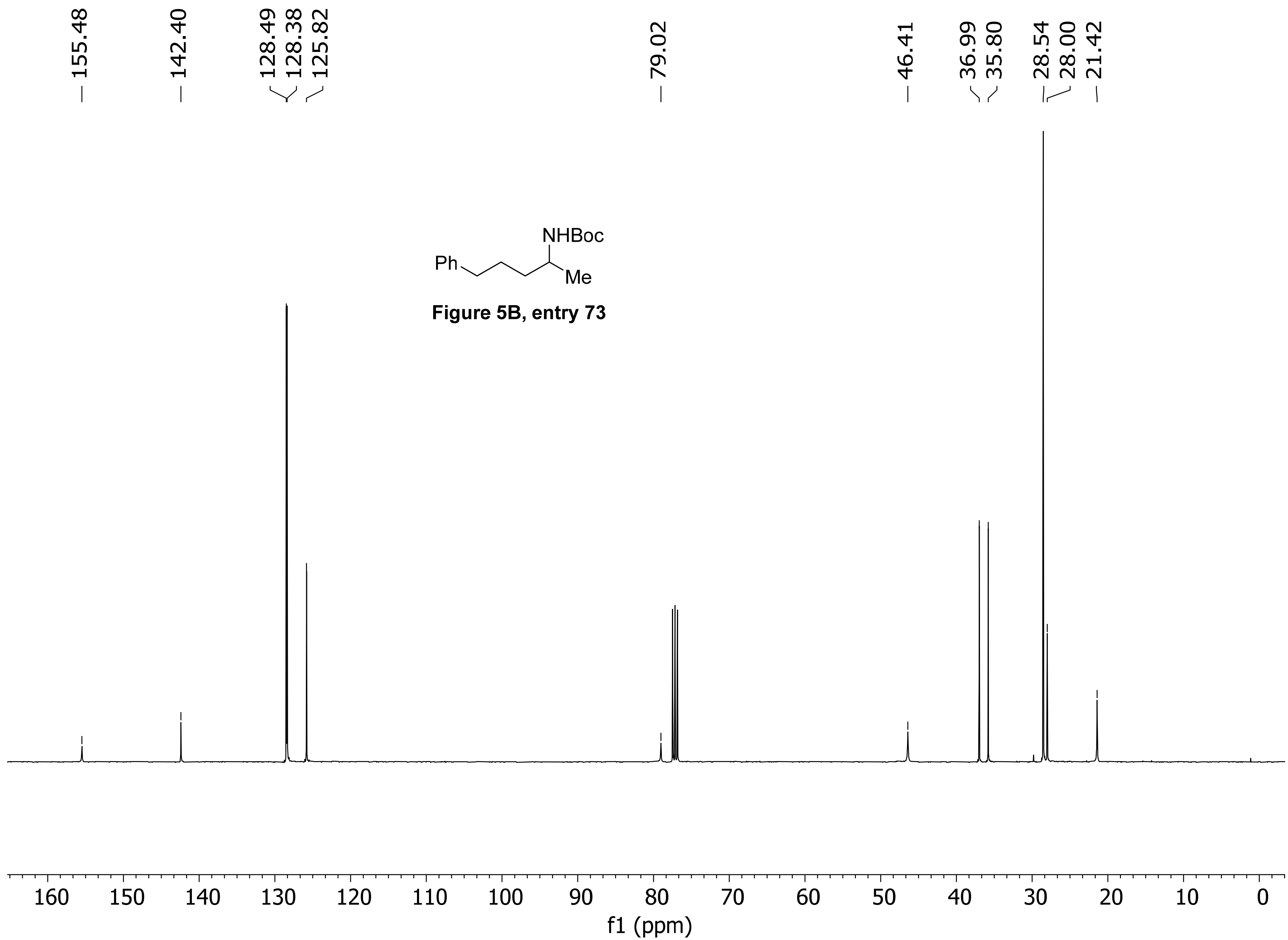


Figure 5B, entry 73

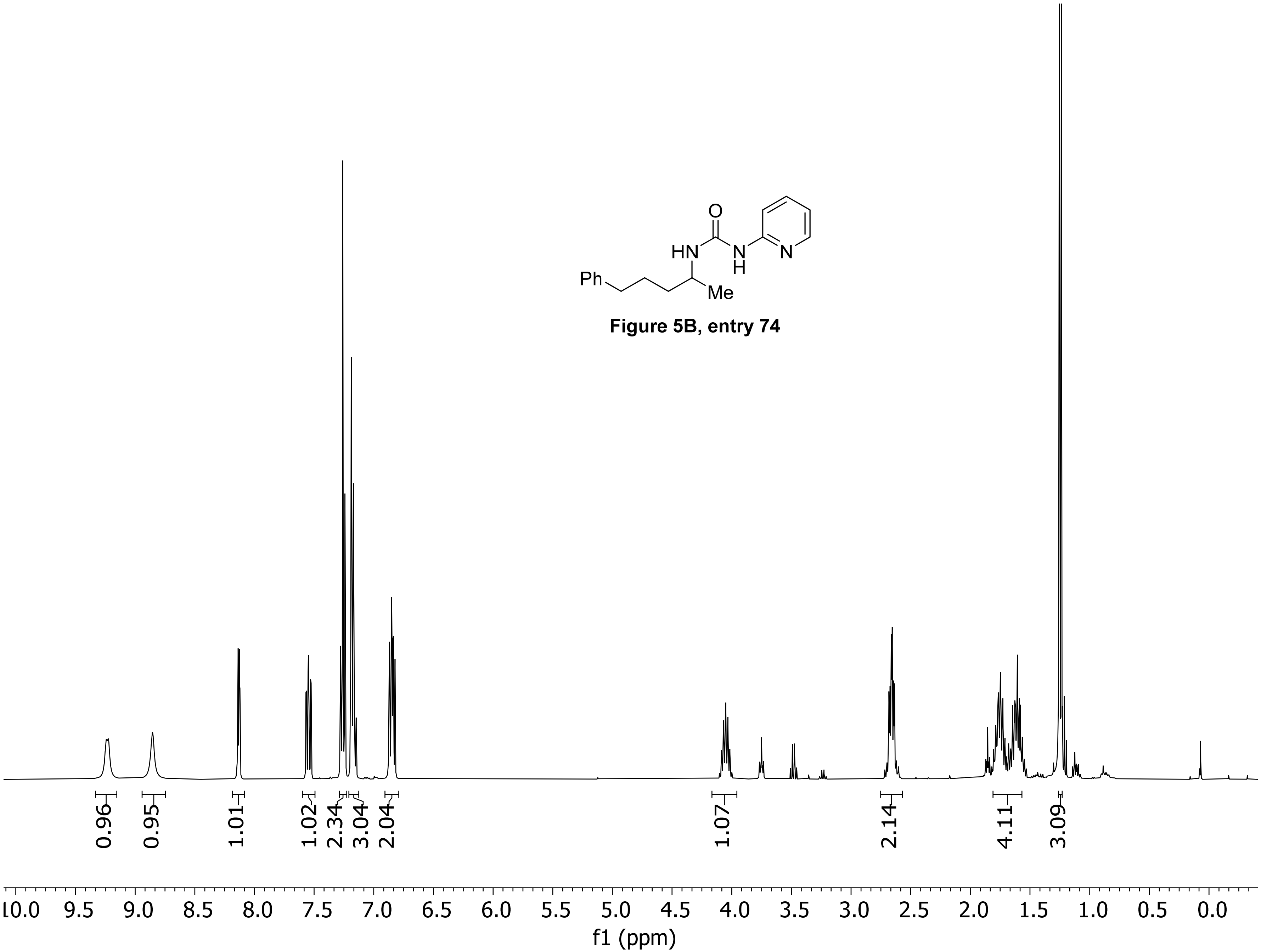
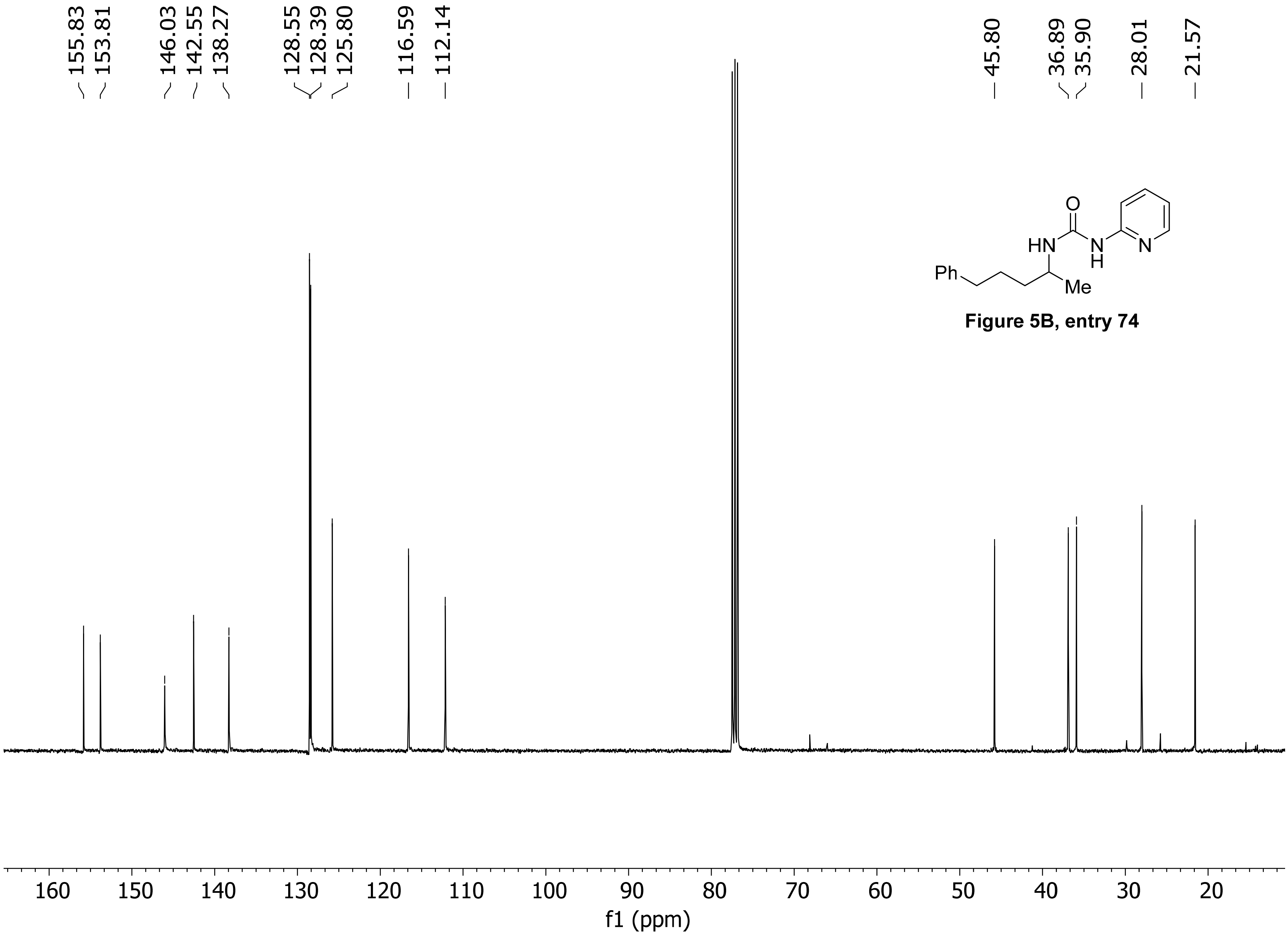
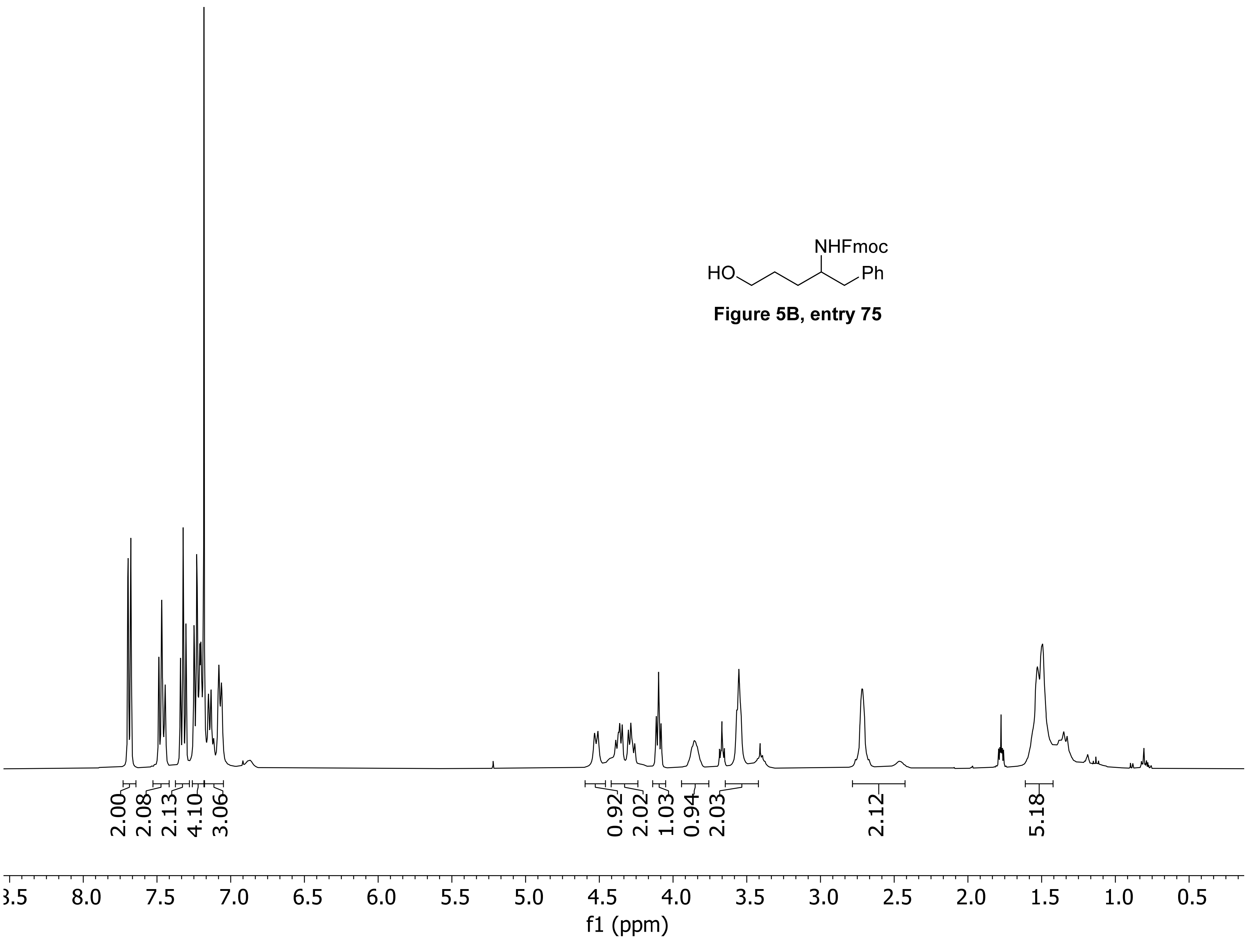


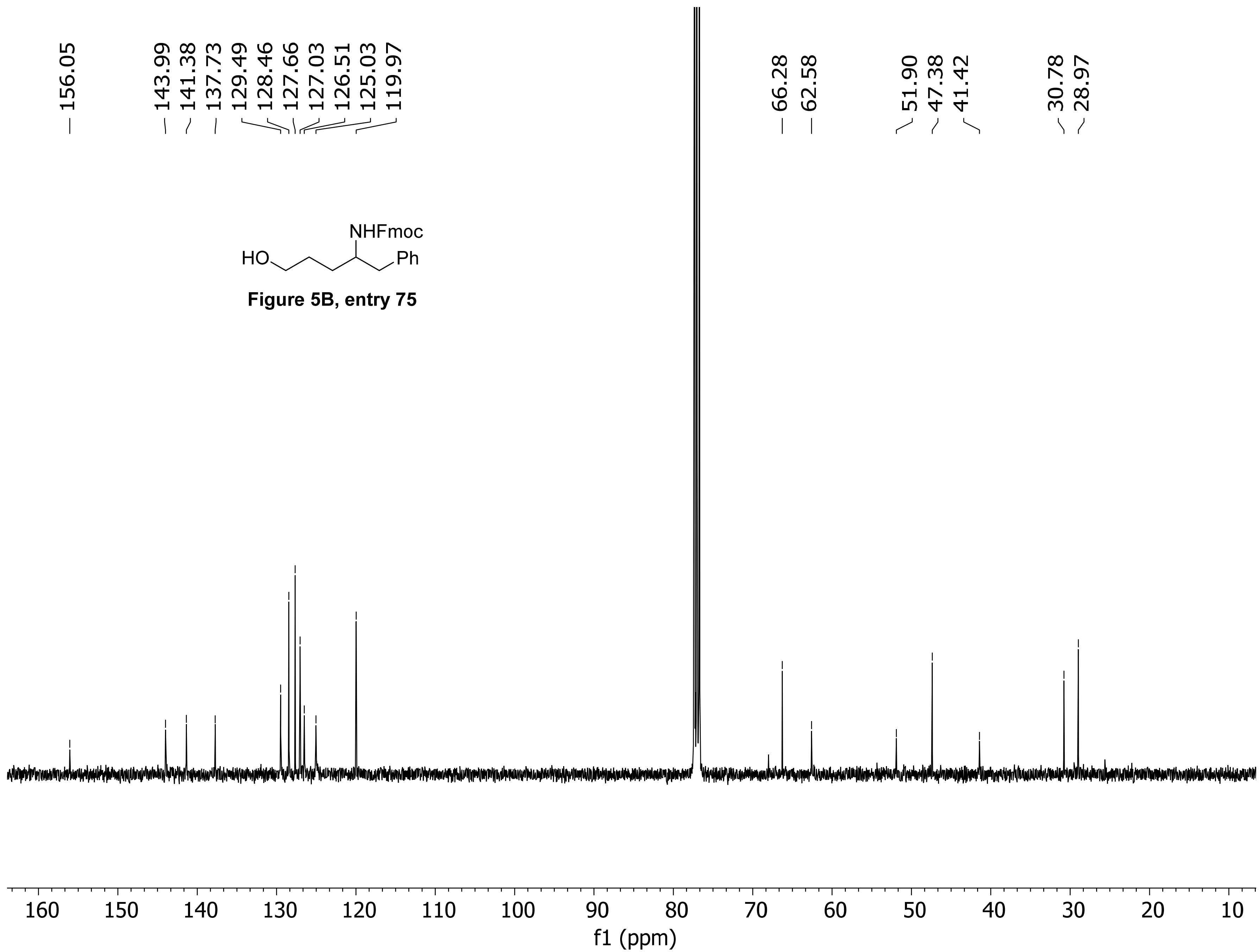
Figure 5B, entry 74

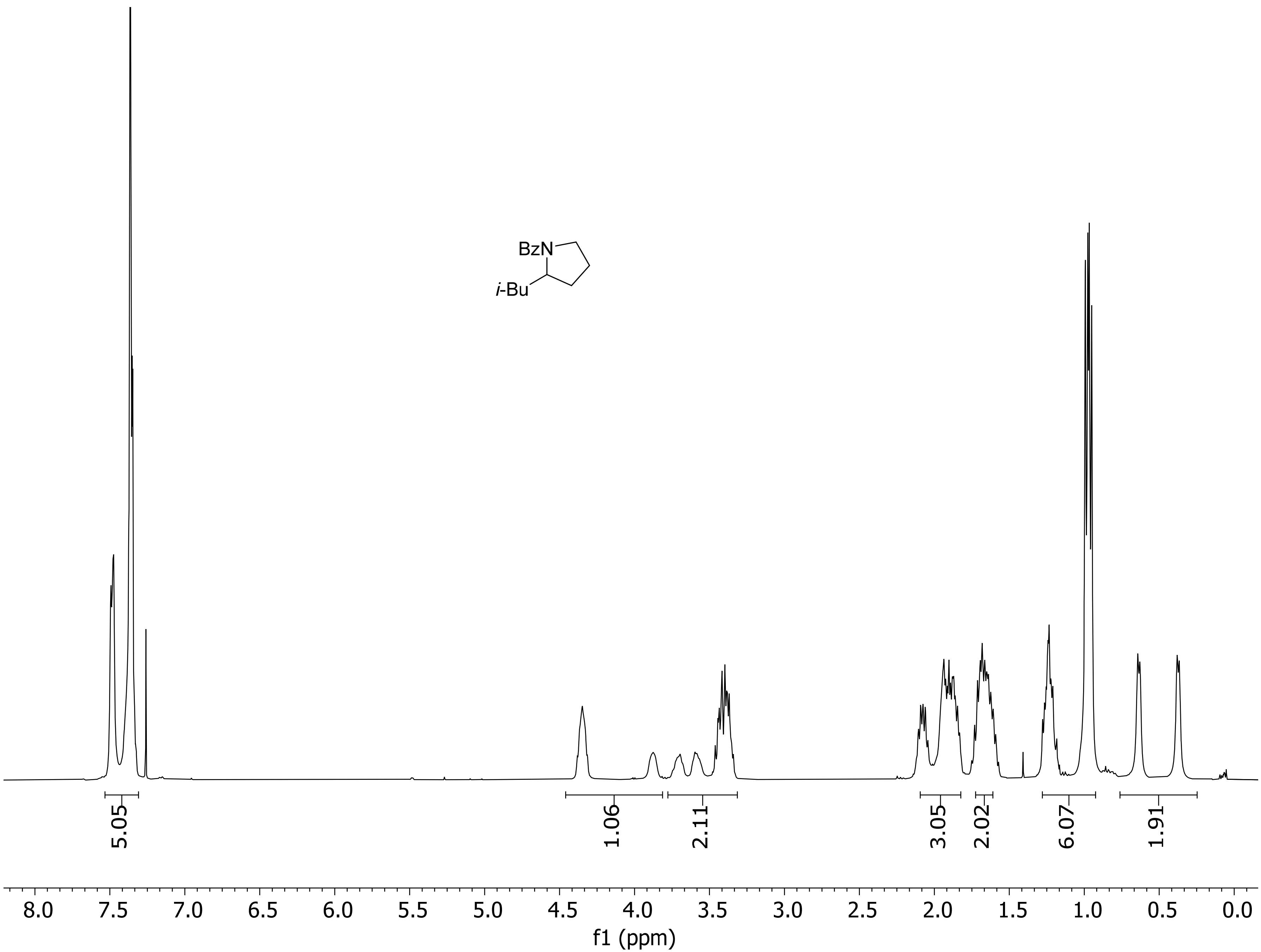


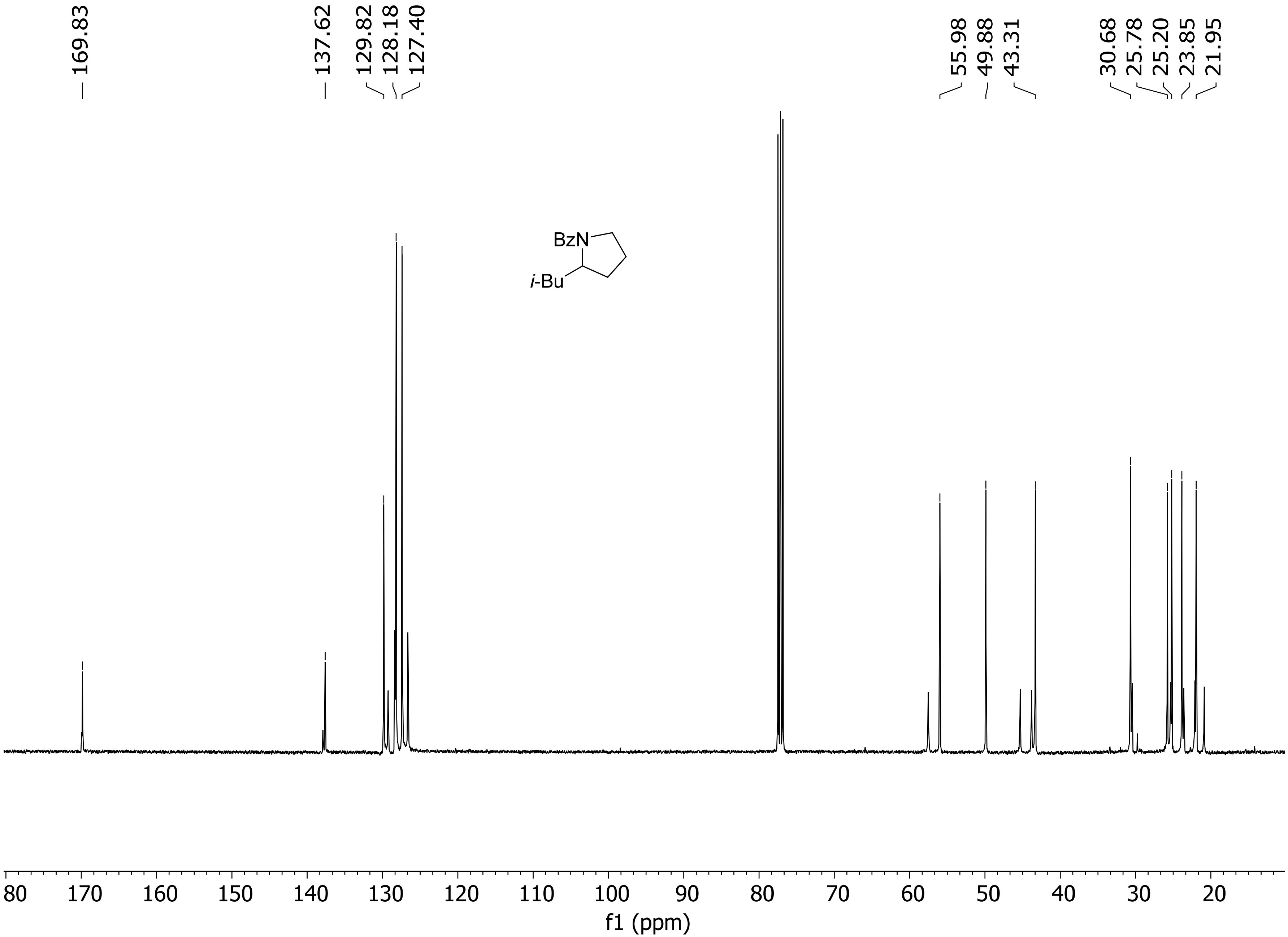
155.83
153.81
146.03
142.55
138.27
128.55
128.39
125.80
116.59
112.14
45.80
36.89
35.90
28.01
21.57
O
HN
N
H
N
Ph
Me
Figure 5B, entry 74
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)



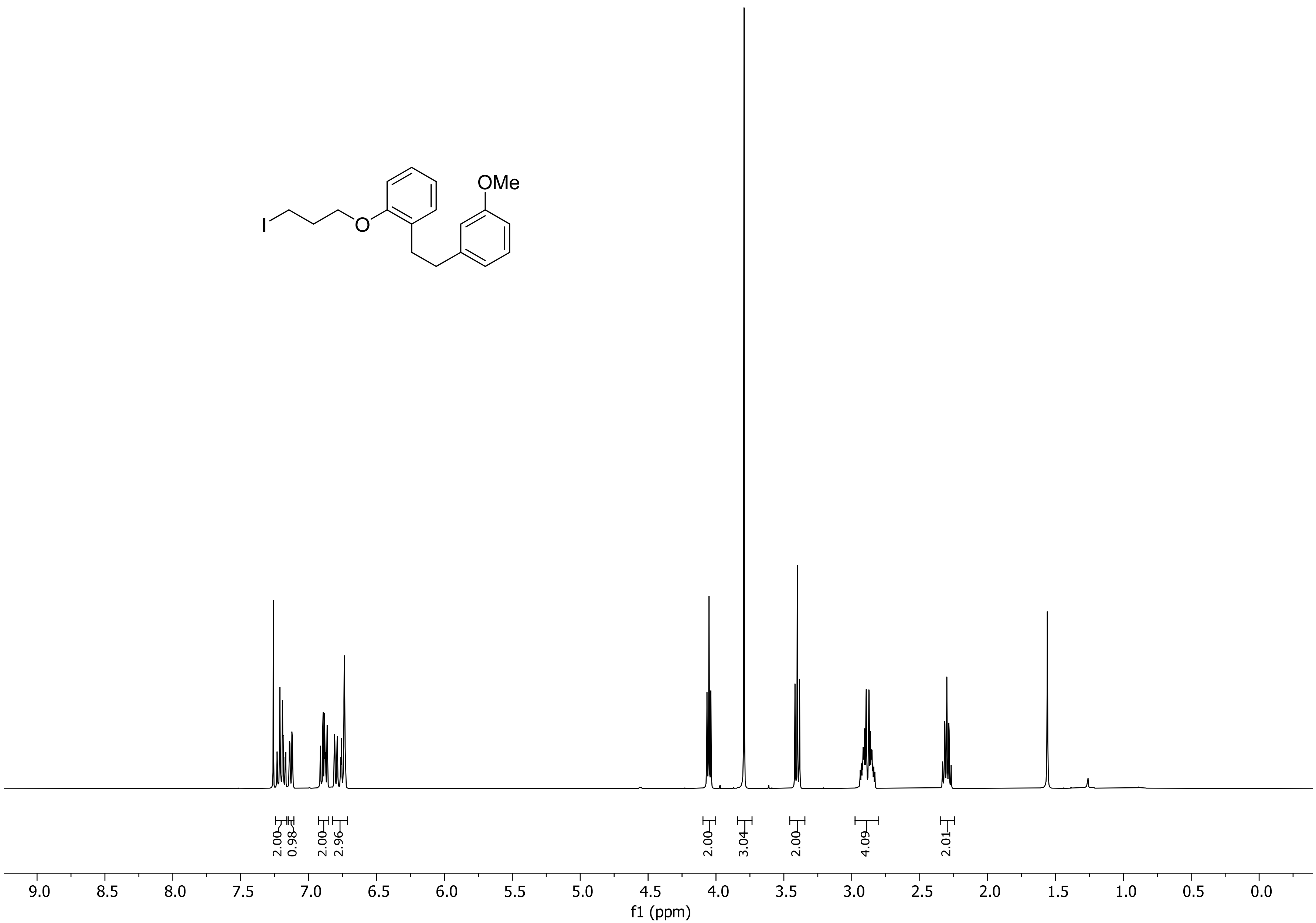
NHFmoc
HO
Ph
Figure 5B, entry 75
2.00
2.08
2.13
4.10
3.06
0.92
2.02
1.03
0.94
2.03
2.12
5.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

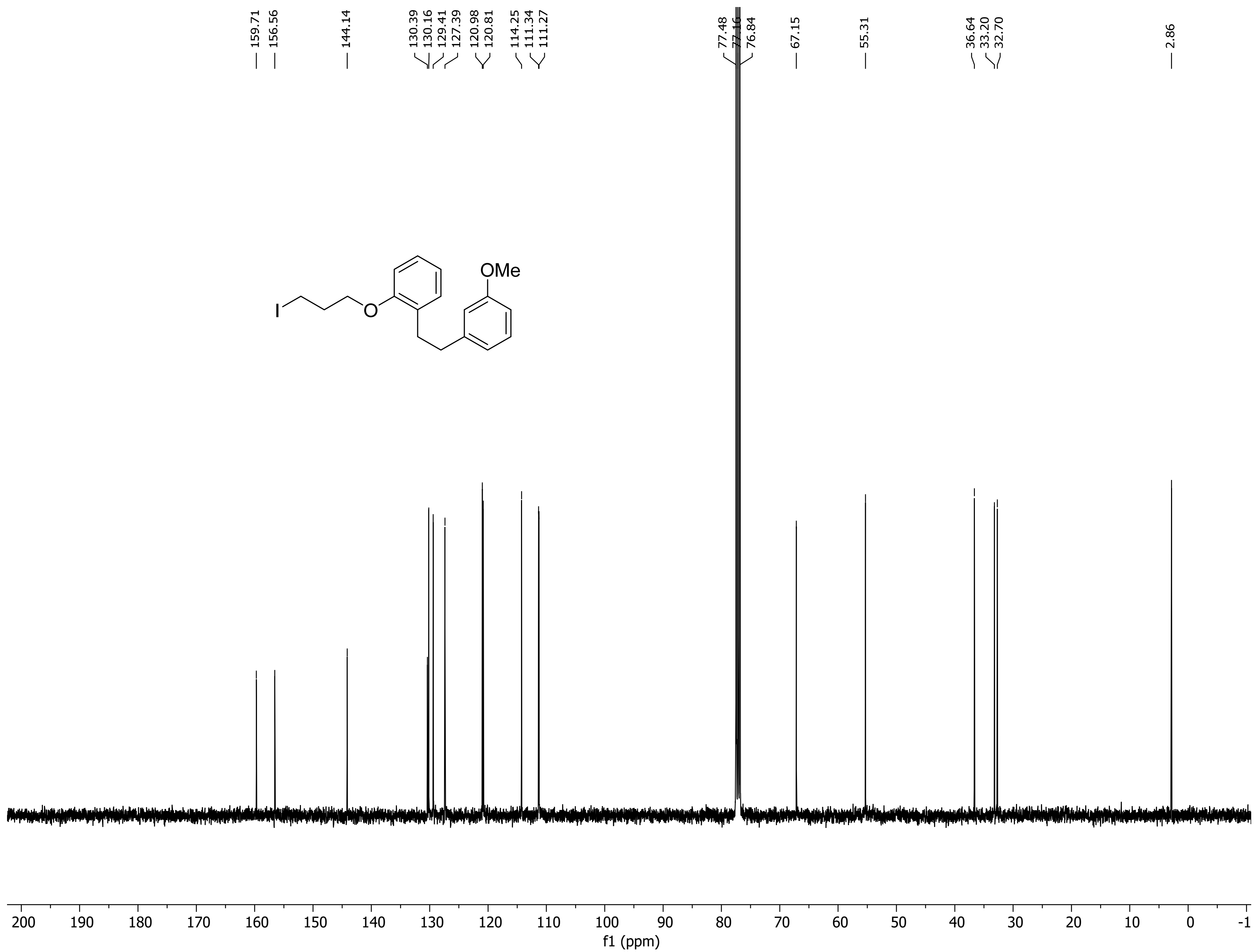

156.05
143.99
141.38
137.73
129.49
128.46
127.66
127.03
126.51
125.03
119.97
66.28
62.58
51.90
47.38
41.42
30.78
28.97
NHFmoc
HO
Ph
Figure 5B, entry 75
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


BzN
i-Bu
5.05
1.06
2.11
3.05
2.02
6.07
1.91
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



169.83
137.62
129.82
128.18
127.40
55.98
49.88
43.31
30.68
25.78
25.20
23.85
21.95
BzN
i-Bu
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


OMe
I
O
2.00
0.98
2.00
2.96
2.00
3.04
2.00
4.09
2.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



159.71
156.56
144.14
130.39
130.16
129.41
127.39
120.98
120.81
114.25
111.34
111.27
77.48
77.16
76.84
67.15
55.31
36.64
33.20
32.70
2.86
OMe
I
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

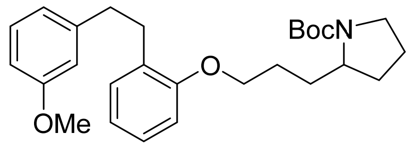
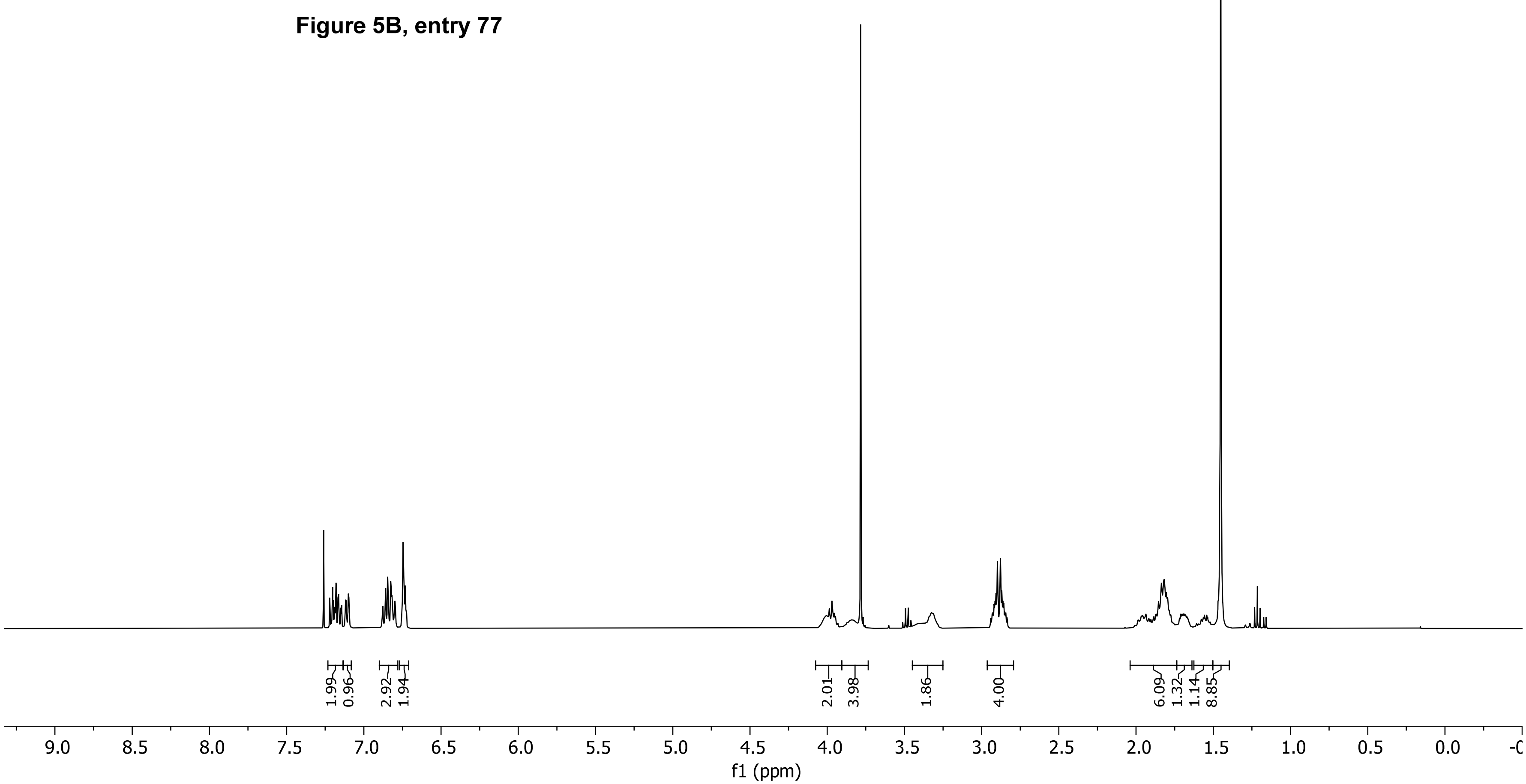


Figure 5B, entry 77



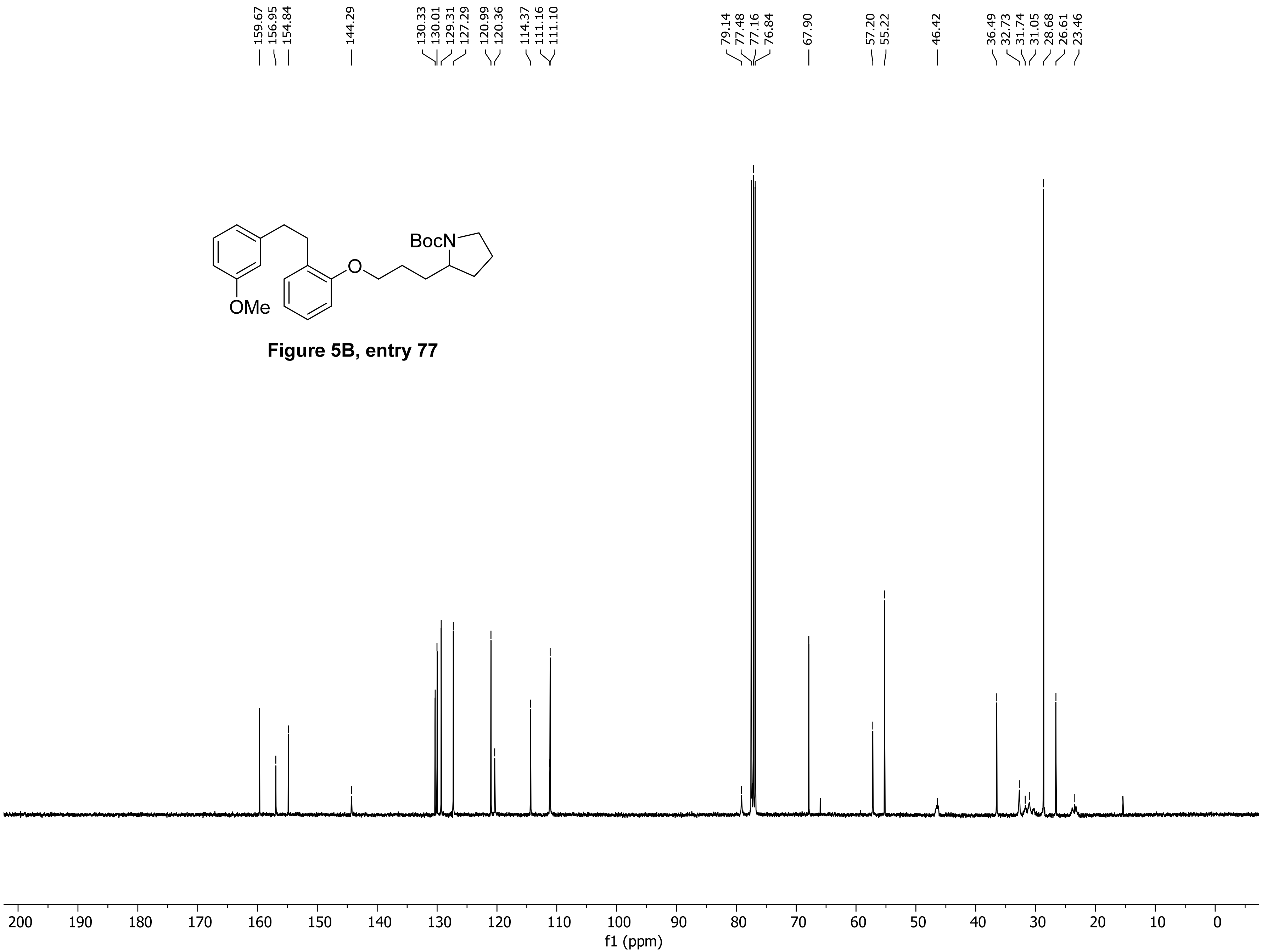


Figure 5B, entry 77

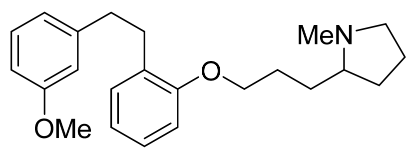
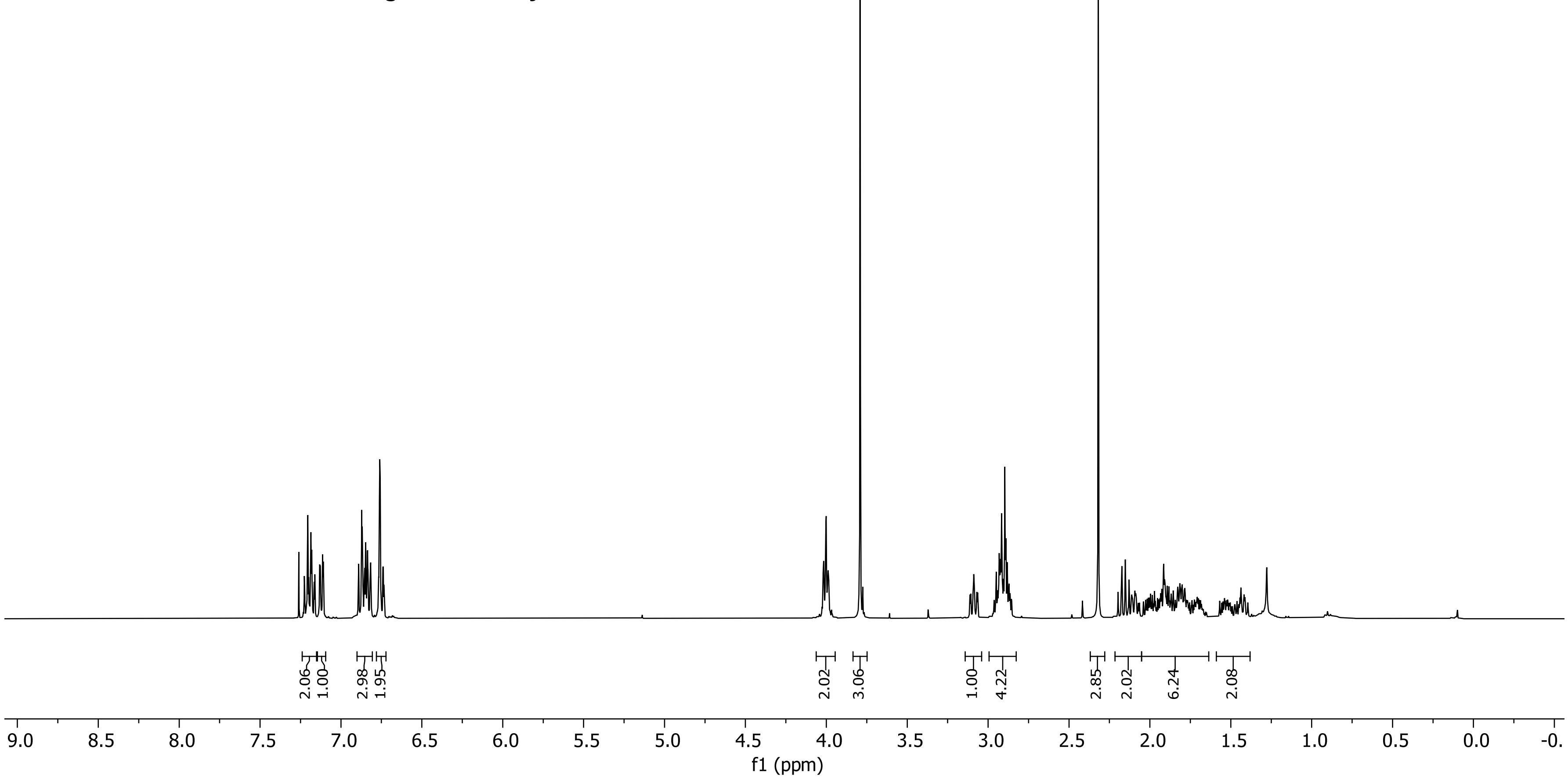


Figure 5B, entry 78



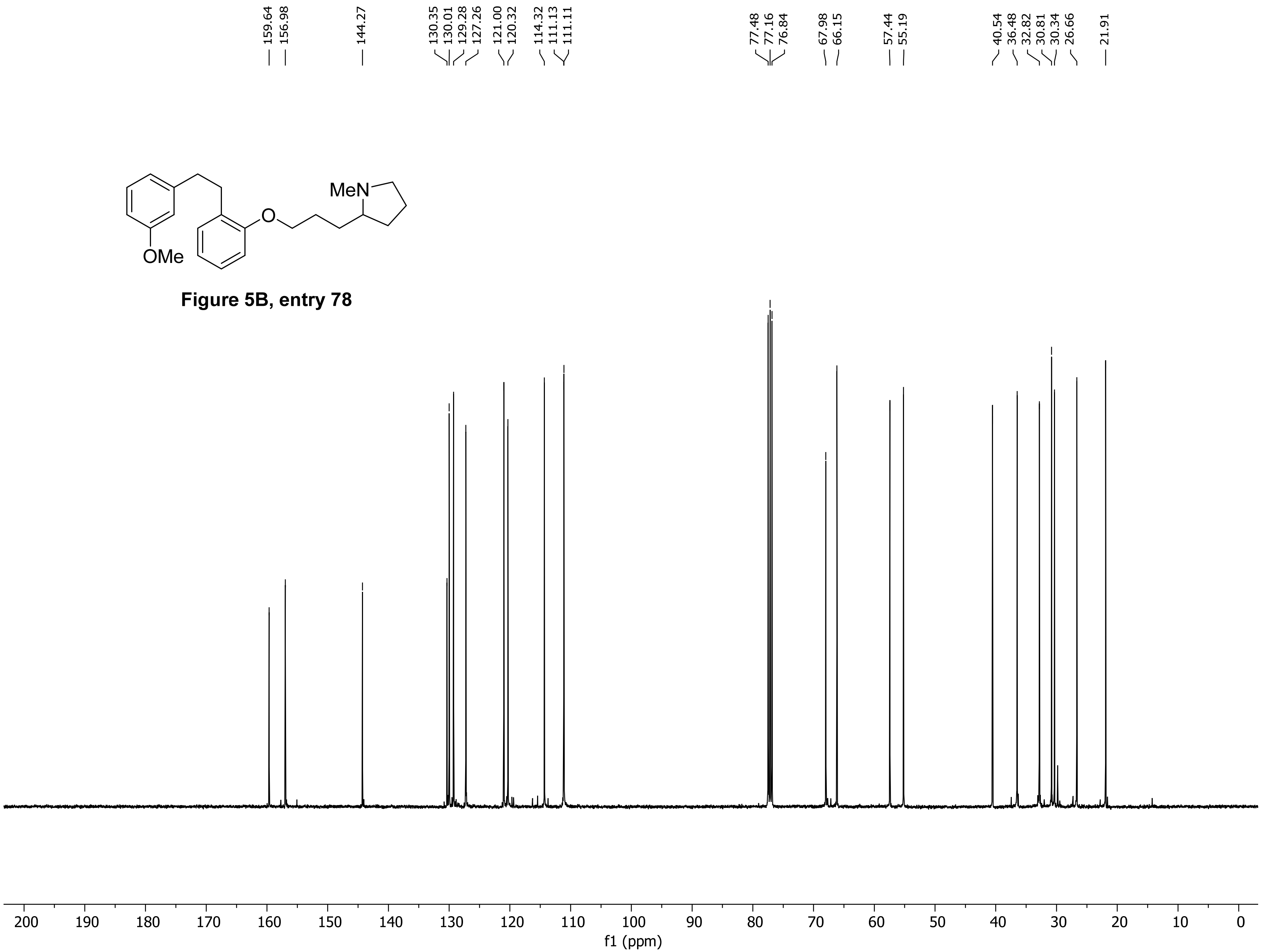


Figure 5B, entry 78

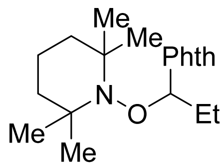
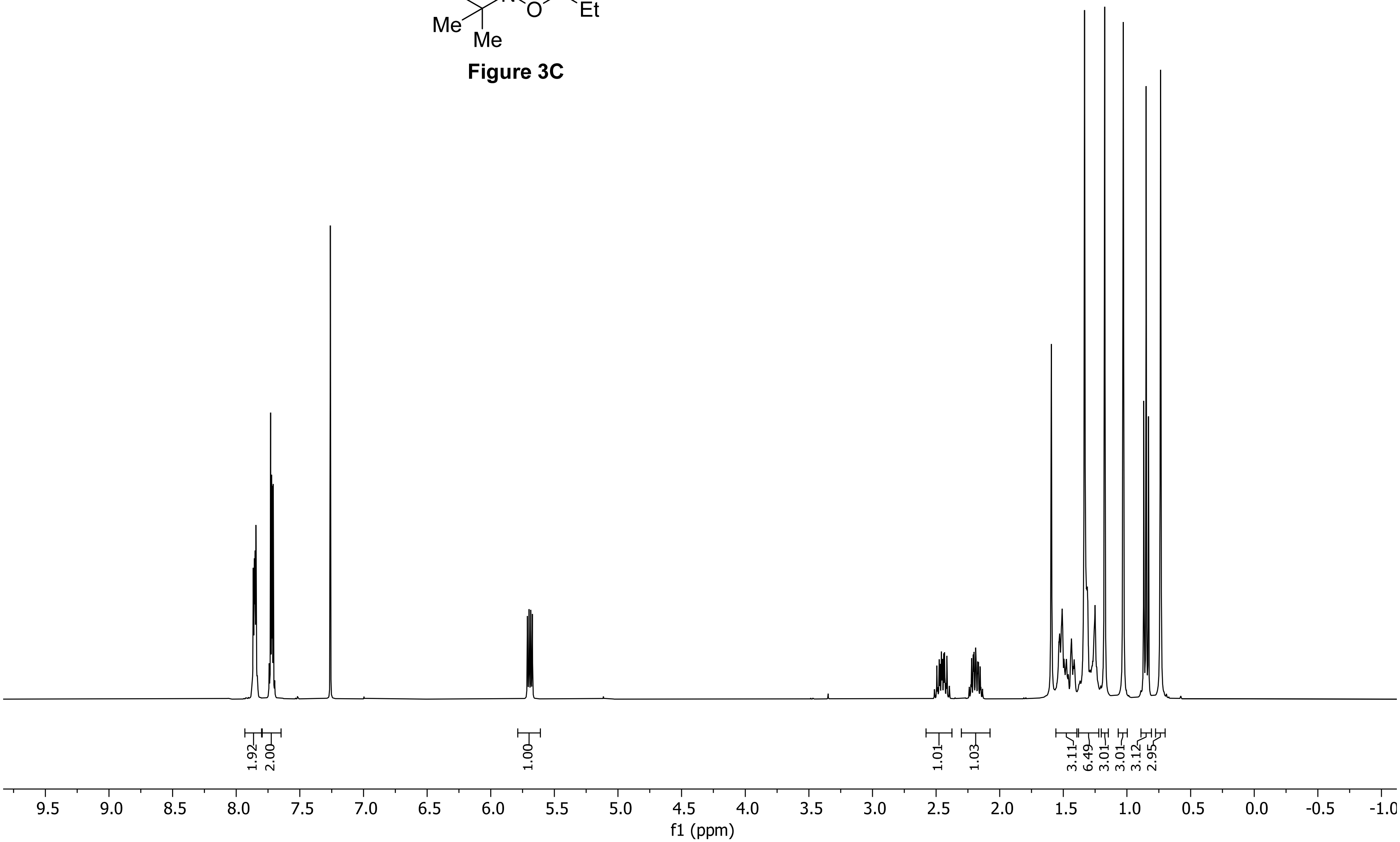
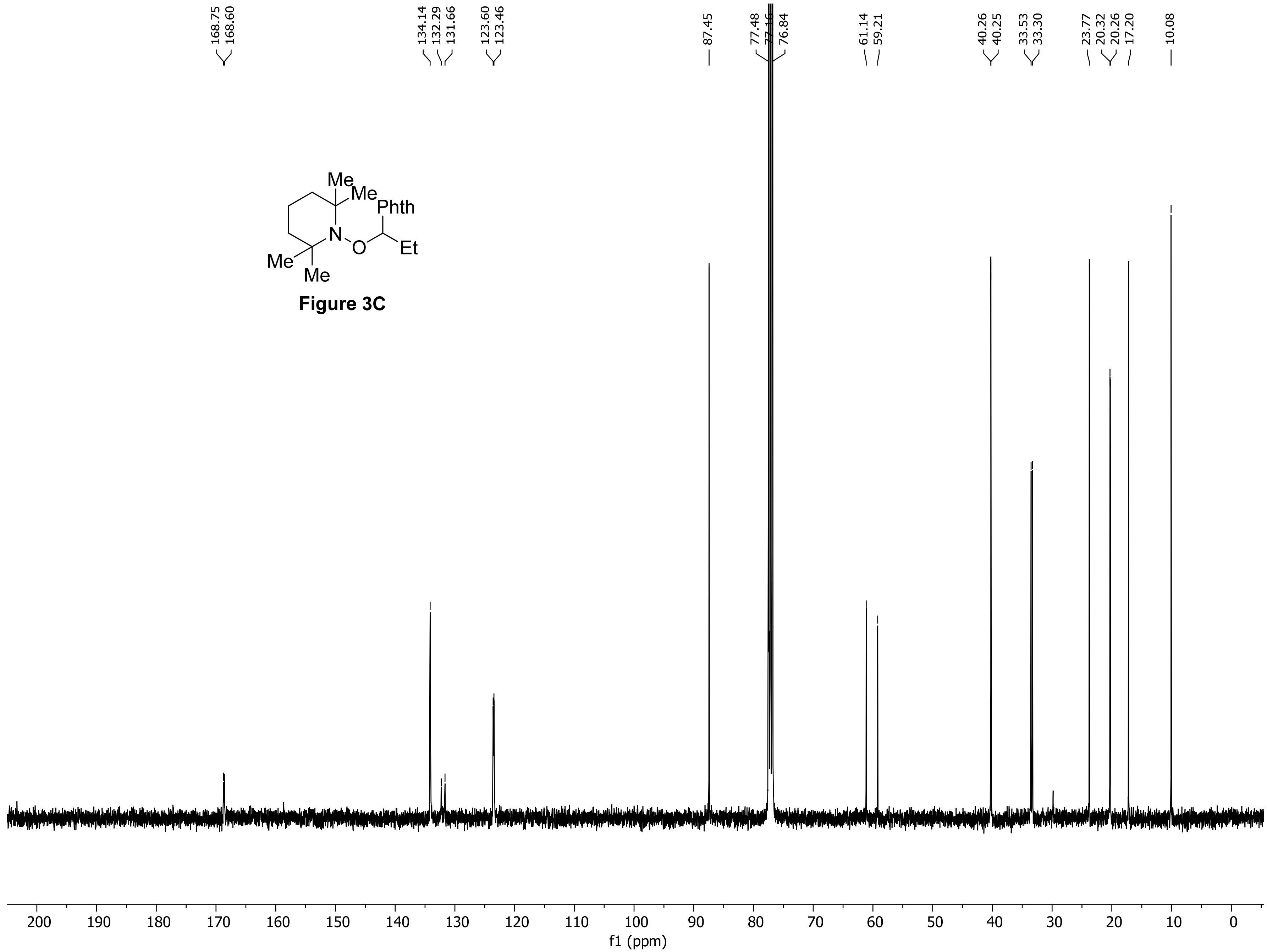

Me
Me
Phth
N
O
Et
Me
Me

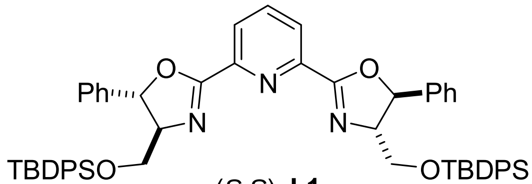
Figure 3C


1.92
2.00
1.00
1.01
1.03
3.11
6.49
3.01
3.01
3.12
2.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



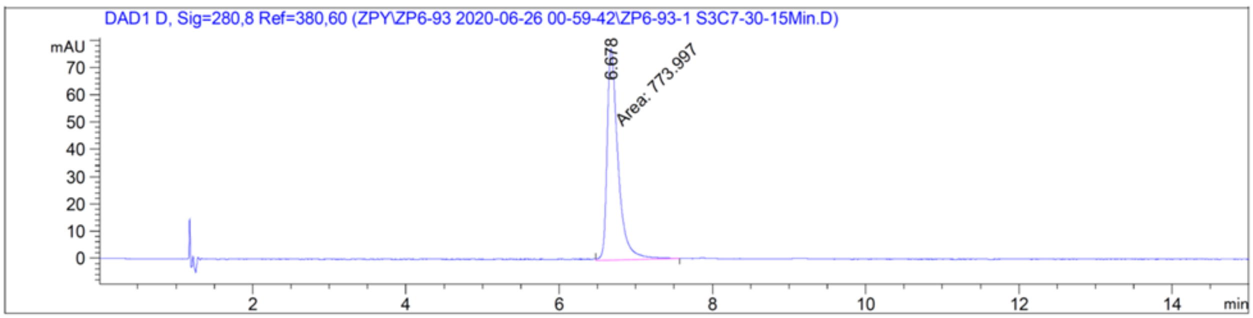
168.75
168.60
134.14
132.29
131.66
123.60
123.46
87.45
77.48
77.16
76.84
61.14
59.21
40.26
40.25
33.53
33.30
23.77
20.32
20.26
17.20
10.08
Figure 3C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Determination of Stereoselectivity

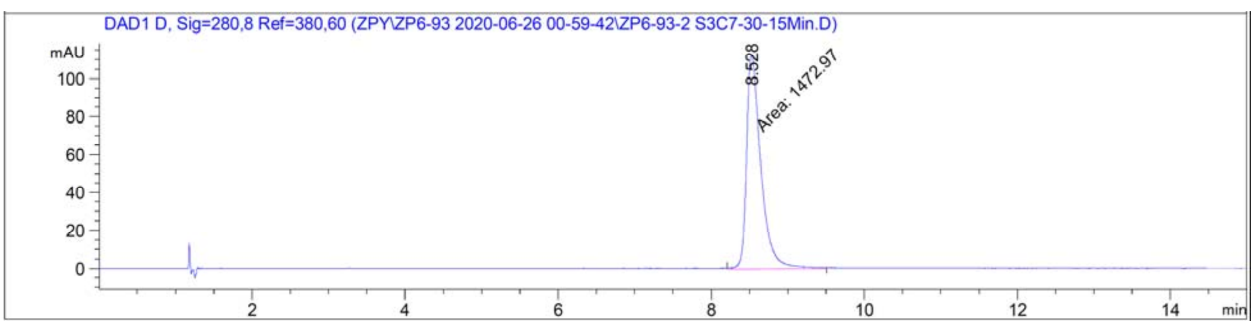


(*S*,*S*)–**L1**

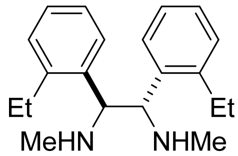
(*S*,*S*)–**L1**: >99% ee
(*R*,*R*)–**L1**: >99% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.678	MM	0.1663	773.99658	77.58902	100.0000

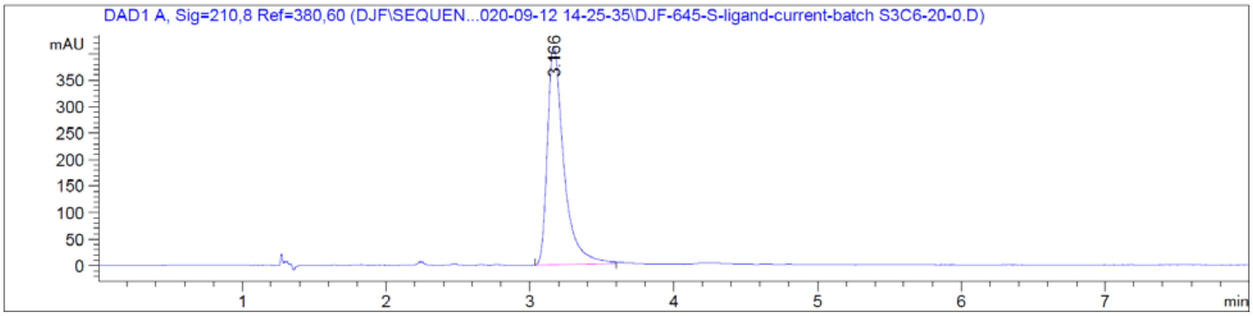


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.528	BB	0.1870	1421.29968	115.11413	100.0000

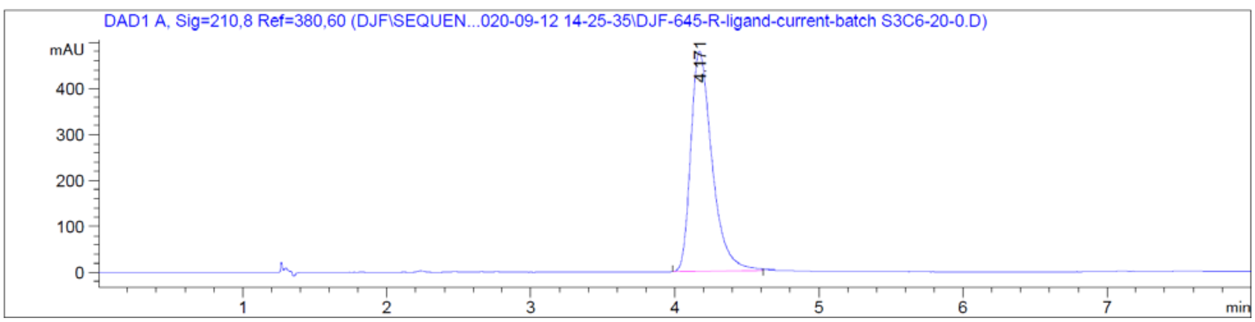


(S,S)–**L2**

(S,S)–**L2**: >99% ee
(R,R)–**L2**: >99% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.166	BB	0.1175	3272.79272	412.97690	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.171	BB	0.1552	4927.75146	478.33942	100.0000

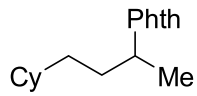
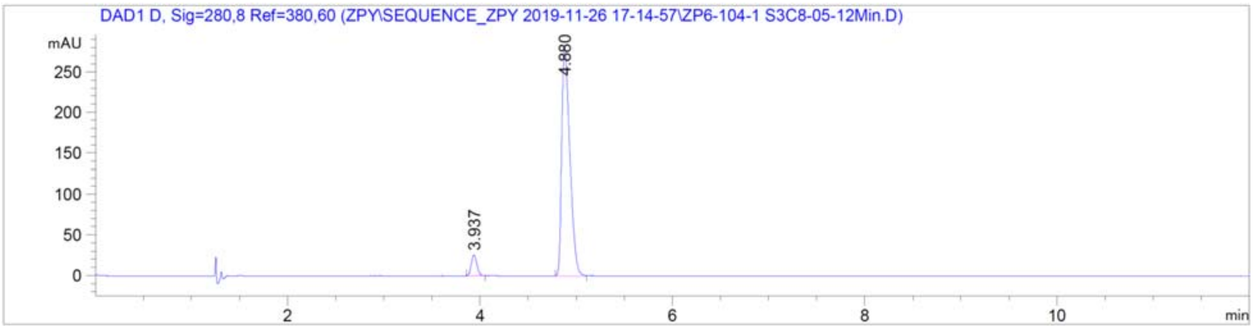
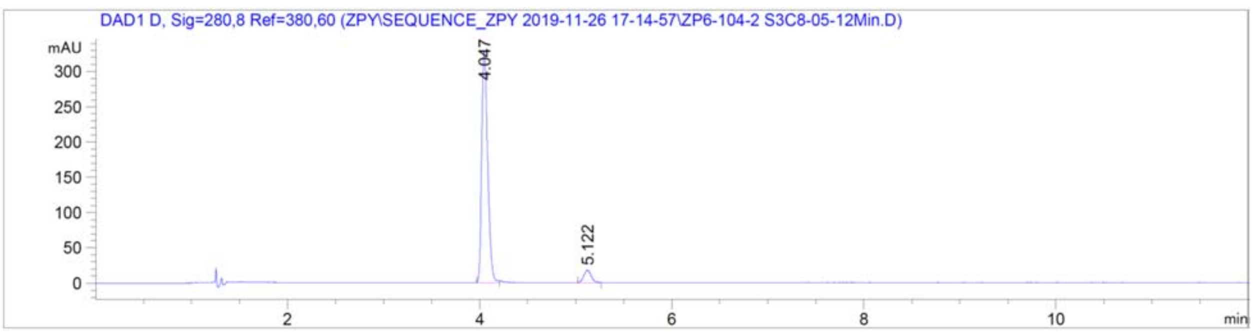


Figure 2B, entry 1

(*S*,*S*)–**L1**: 88% ee
(*R*,*R*)–**L1**: 88% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.937	BB	0.0635	104.04684	25.54880	5.8999
2	4.880	BB	0.0895	1659.48596	282.47015	94.1001



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.047	BB	0.0663	1416.82642	328.93582	93.8165
2	5.122	BB	0.0818	93.38371	17.63088	6.1835

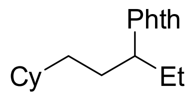
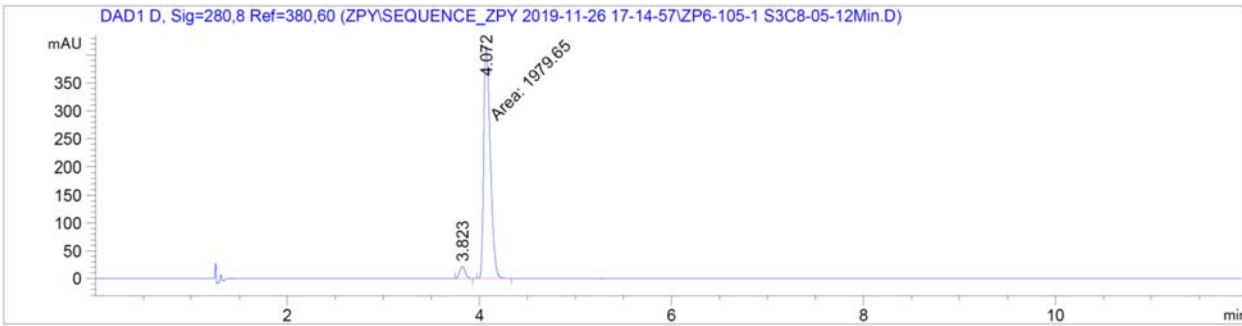
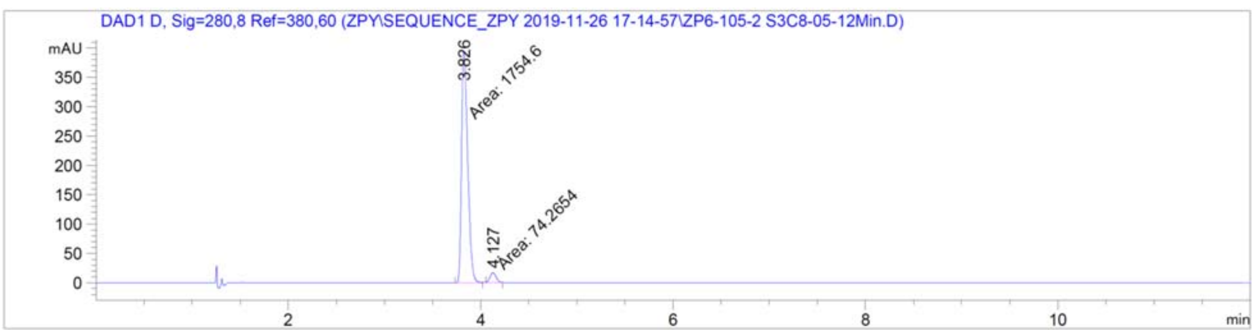


Figure 2B, entry 2

(*S*,*S*)–**L1**: 92% ee
(*R*,*R*)–**L1**: 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.823	BB	0.0617	87.25160	21.81968	4.2214
2	4.072	MM	0.0793	1979.65356	415.99155	95.7786



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.826	MM	0.0741	1754.59705	394.58246	95.9393
2	4.127	MM	0.0739	74.26545	16.75755	4.0607

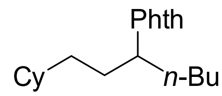
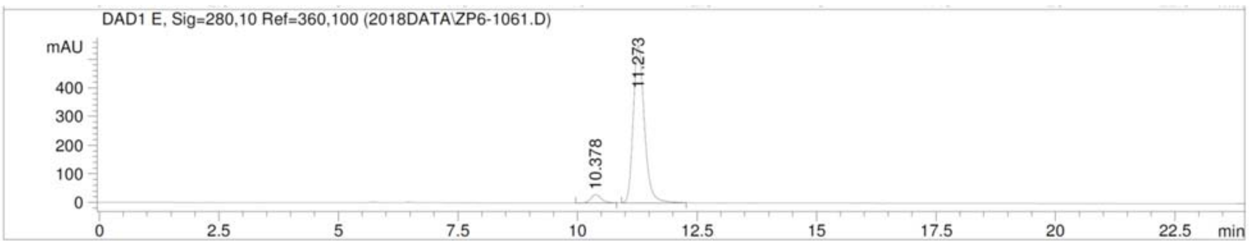
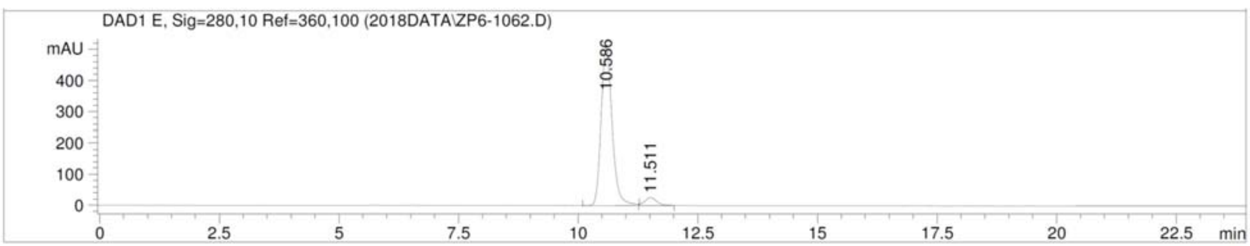


Figure 2B, entry 3

(*S*,*S*)–**L1**: 91% ee
(*R*,*R*)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.378	PB	0.2291	441.36435	29.07626	4.7251
2	11.273	BB	0.2464	8899.42871	551.12250	95.2749



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.586	VB	0.2449	8168.14355	509.77371	94.8184
2	11.511	BB	0.2613	446.37003	25.86475	5.1816

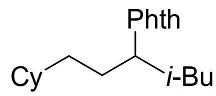
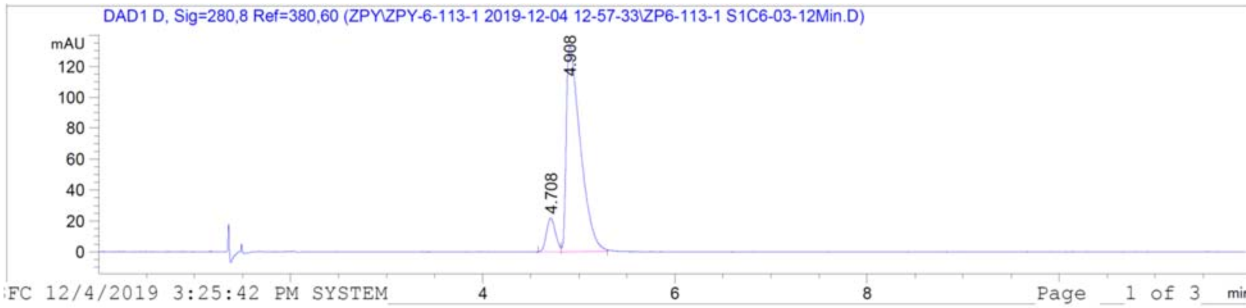
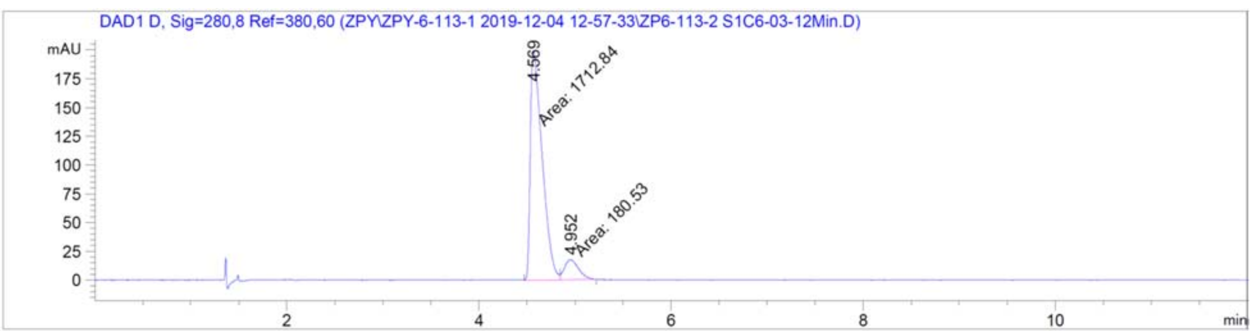


Figure 2B, entry 4

(*S*,*S*)–**L1**: 81% ee
(*R*,*R*)–**L1**: 81% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.708	BV	0.1027	142.53195	21.68252	9.4900
2	4.908	VB	0.1510	1359.39075	133.28262	90.5100



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.569	MF	0.1437	1712.83997	198.66531	90.4652
2	4.952	FM	0.1720	180.52959	17.49235	9.5348

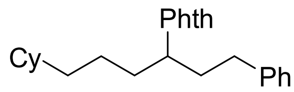
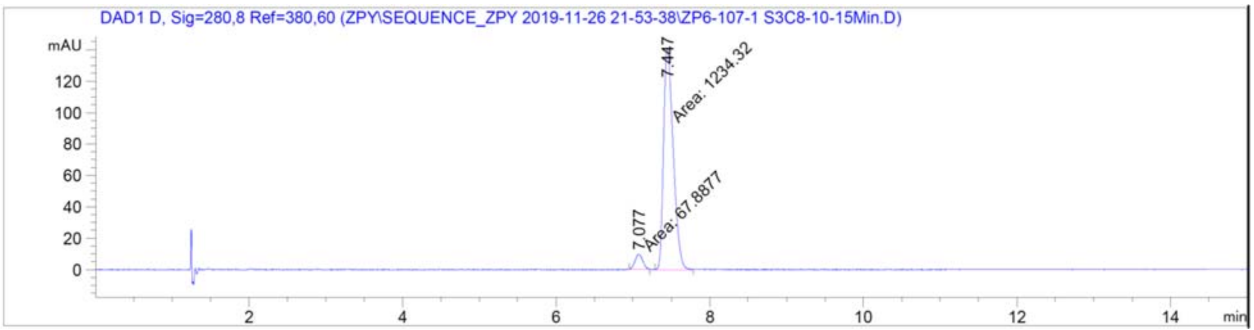
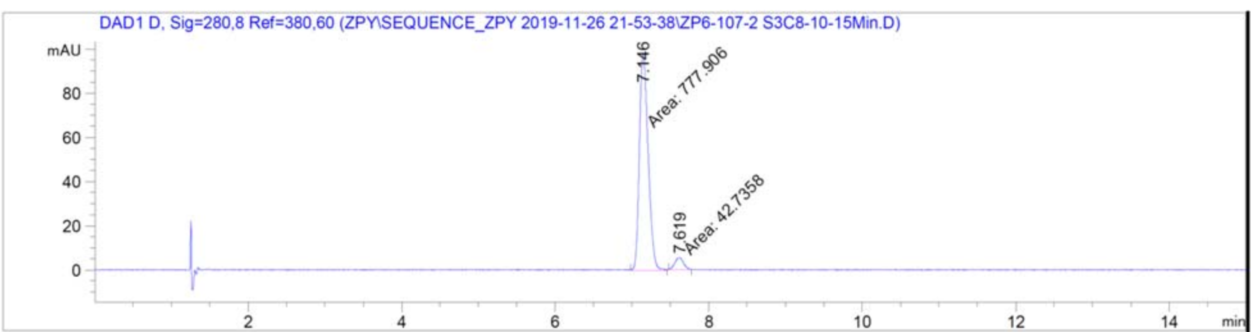


Figure 2B, entry 5

(*S*,*S*)–**L1**: 90% ee
(*R*,*R*)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.077	MM	0.1188	67.88775	9.52756	5.2133
2	7.447	MM	0.1459	1234.32483	140.99261	94.7867



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.146	MM	0.1319	777.90594	98.26344	94.7924
2	7.619	MM	0.1330	42.73585	5.35734	5.2076

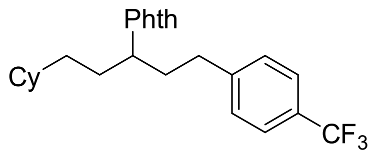
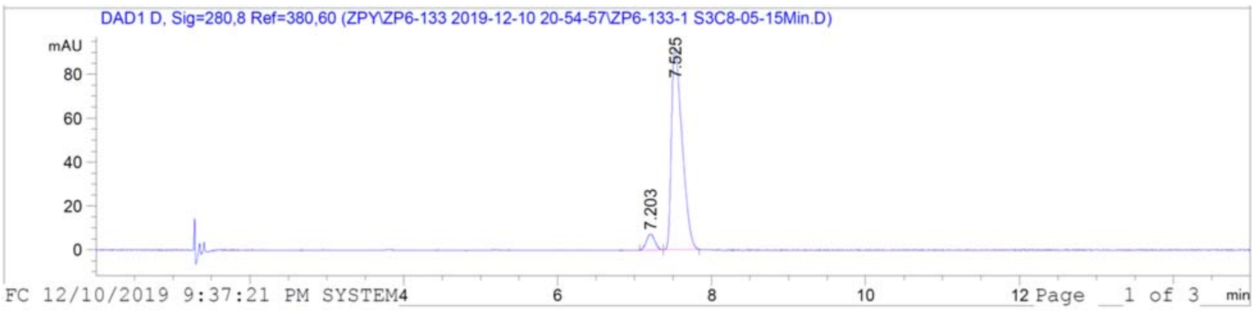
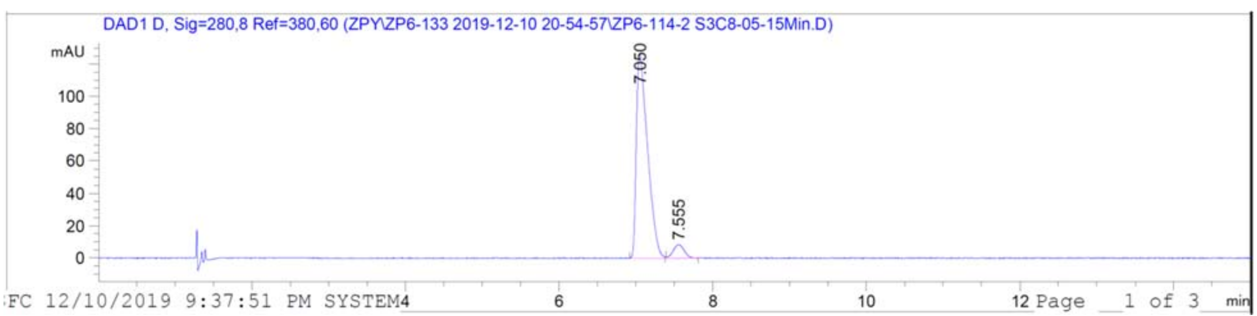


Figure 2B, entry 6

(*S*,*S*)–**L1**: 88% ee
(*R*,*R*)–**L1**: 88% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.203	BV	0.1047	55.71856	7.16634	5.8809
2	7.525	VB	0.1449	891.72821	92.14342	94.1191



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.050	BB	0.1471	1283.31323	126.72497	93.8947
2	7.555	BB	0.1448	83.44483	8.47795	6.1053

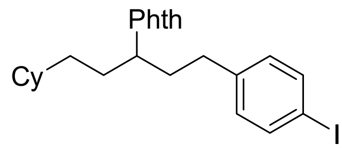
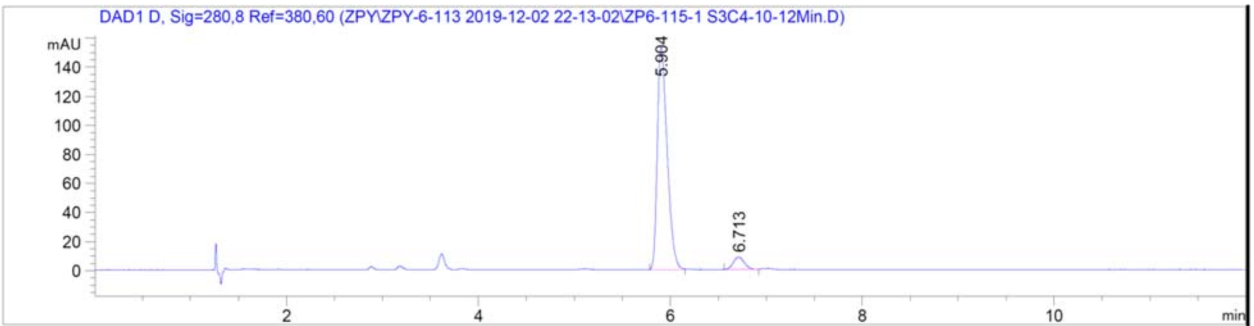
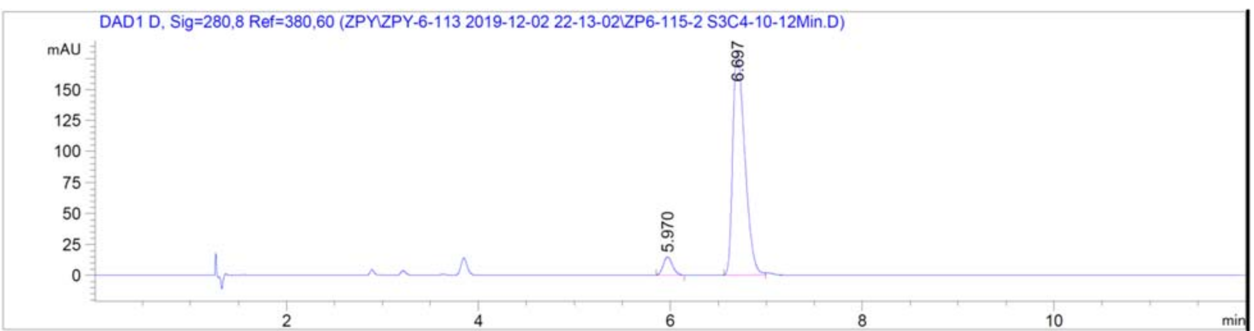


Figure 2B, entry 7

(*S*,*S*)–**L1**: 89% ee
(*R*,*R*)–**L1**: 88% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.904	BB	0.1103	1092.87805	153.01134	94.3436
2	6.713	BB	0.1195	65.52425	8.44588	5.6564



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.970	BB	0.1033	100.12148	14.92236	5.9975
2	6.697	BB	0.1348	1569.26477	179.81598	94.0025

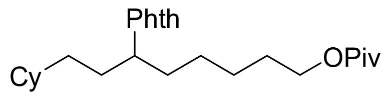
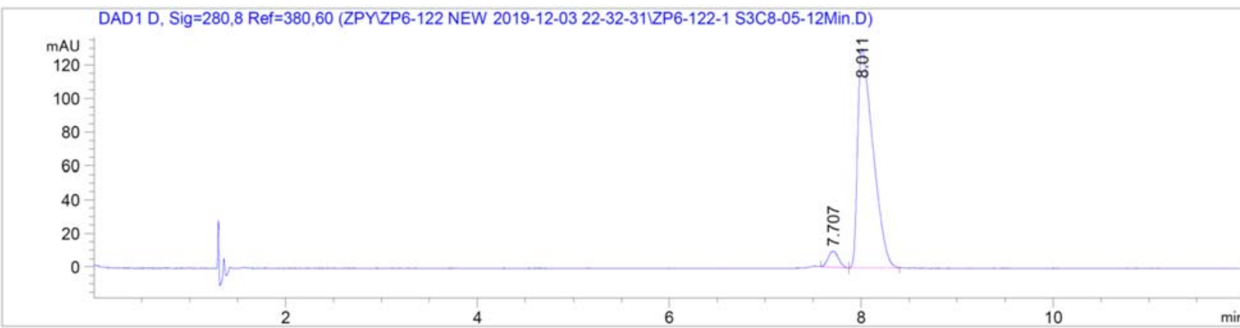
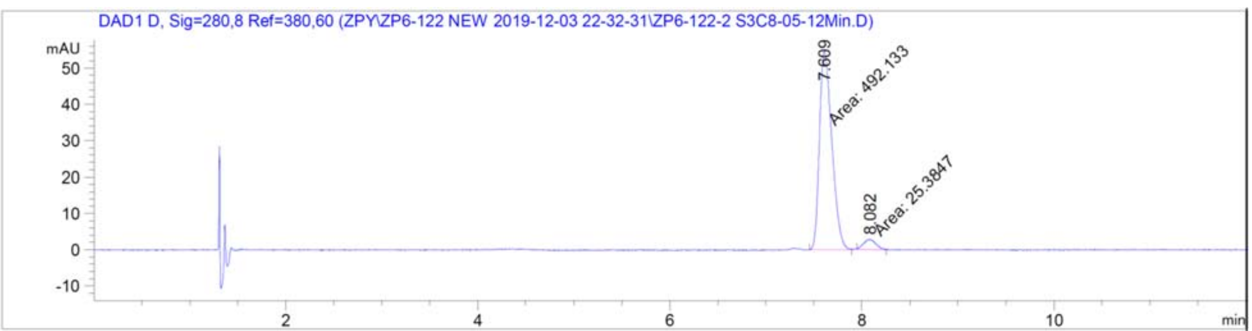


Figure 2B, entry 8

(S,S)–**L1**: 90% ee
(R,R)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.707	BV	0.1123	73.34638	9.80177	4.8086
2	8.011	VB	0.1671	1451.96252	130.16167	95.1914



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.609	MM	0.1500	492.13345	54.69331	95.0949
2	8.082	MM	0.1513	25.38474	2.79612	4.9051

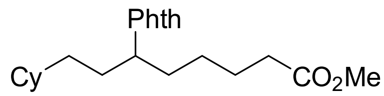
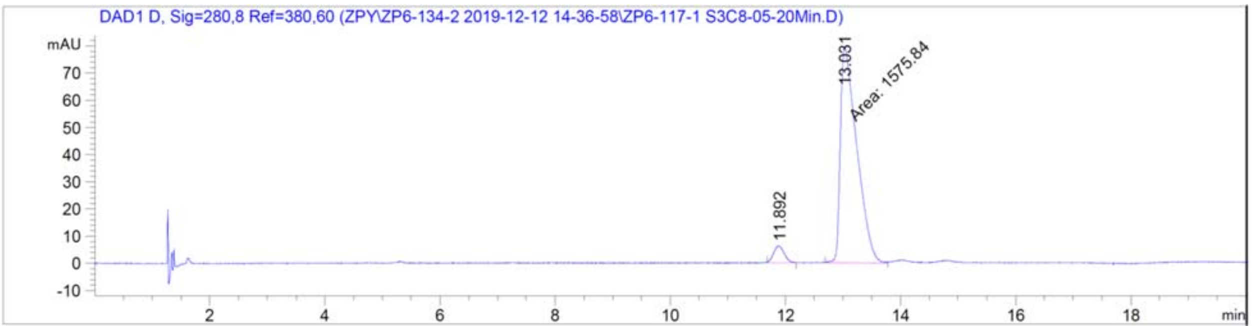
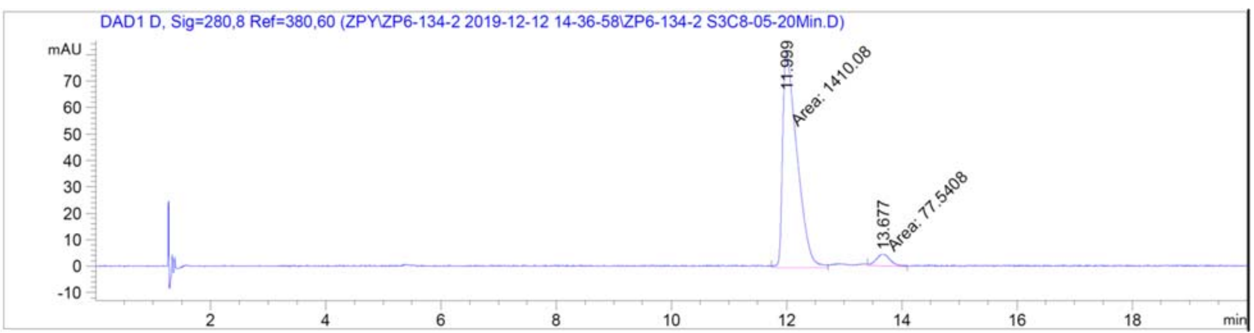


Figure 2B, entry 9

(S,S)–**L1**: 91% ee
(R,R)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.892	BB	0.1514	77.35738	6.16347	4.6793
2	13.031	MM	0.3308	1575.83728	79.39937	95.3207



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.999	MM	0.2883	1410.07910	81.51436	94.7876
2	13.677	MM	0.2890	77.54079	4.47122	5.2124

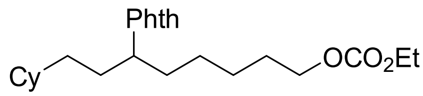
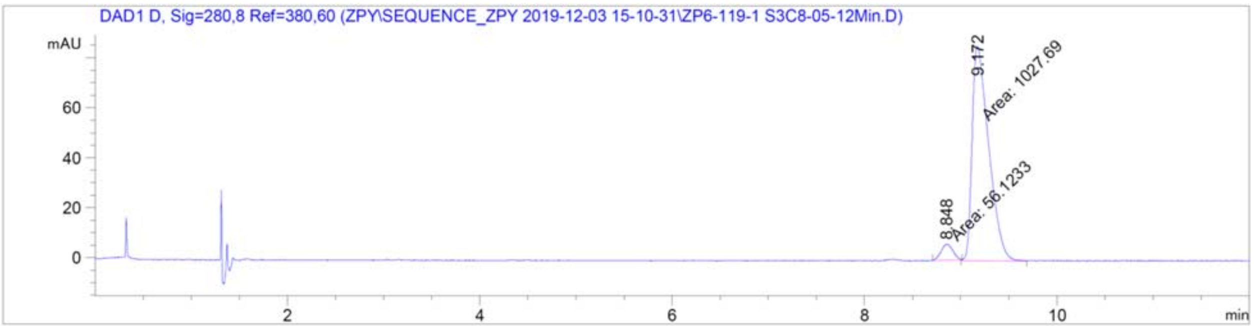
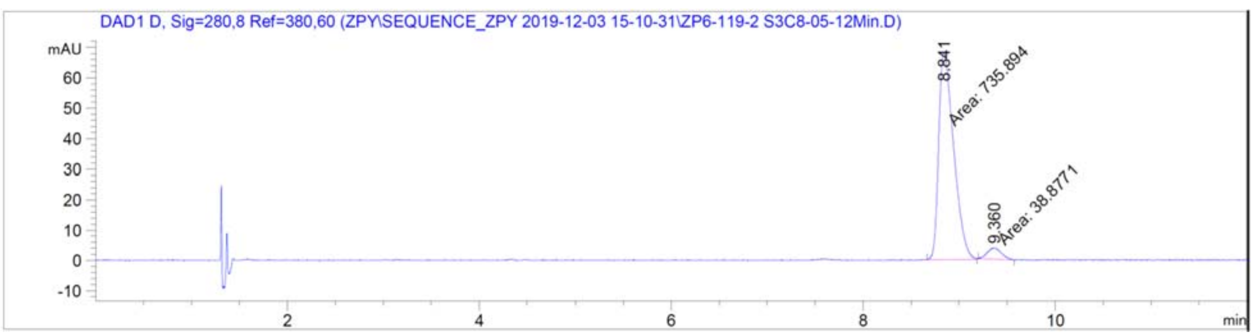


Figure 2B, entry 10

(*S*,*S*)–**L1**: 90% ee
(*R*,*R*)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.848	MM	0.1456	56.12333	6.42433	5.1783
2	9.172	MM	0.1999	1027.68787	85.68991	94.8217



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.841	MM	0.1797	735.89423	68.26038	94.9821
2	9.360	MM	0.1772	38.87712	3.65649	5.0179

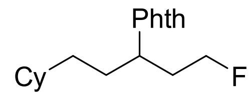
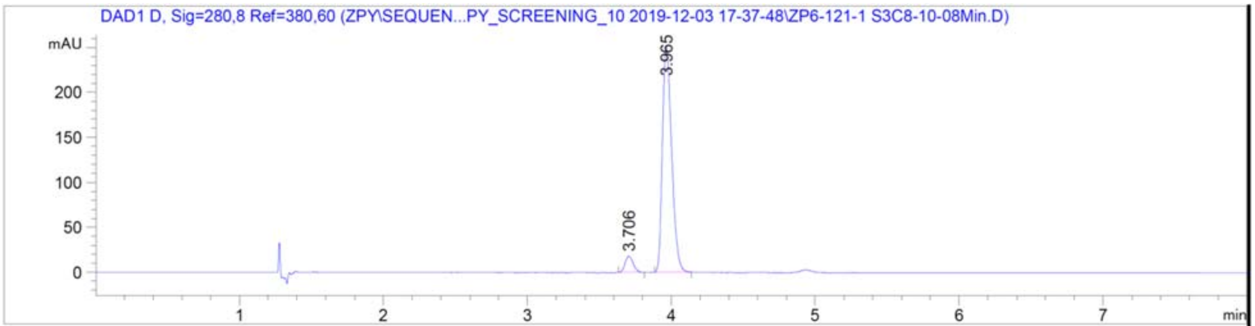
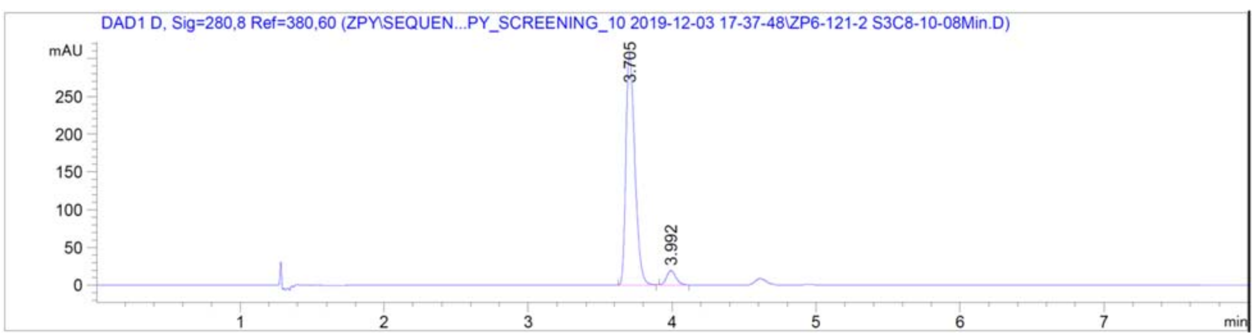


Figure 2B, entry 11

(*S*,*S*)–**L1**: 88% ee
(*R*,*R*)–**L1**: 88% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.706	BB	0.0613	73.16360	18.43524	6.0872
2	3.965	BB	0.0704	1128.76807	251.47113	93.9128



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.705	BB	0.0674	1326.66492	306.79745	93.8497
2	3.992	BB	0.0698	86.94036	19.20261	6.1503

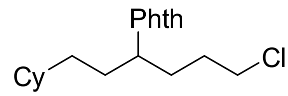
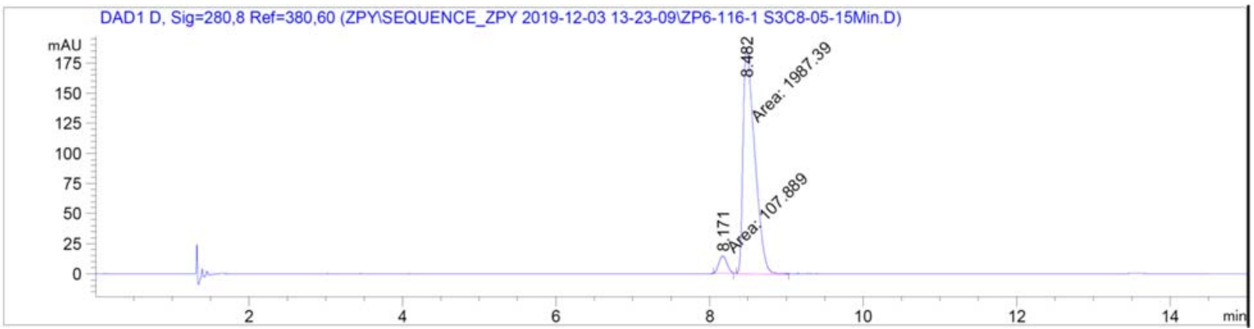
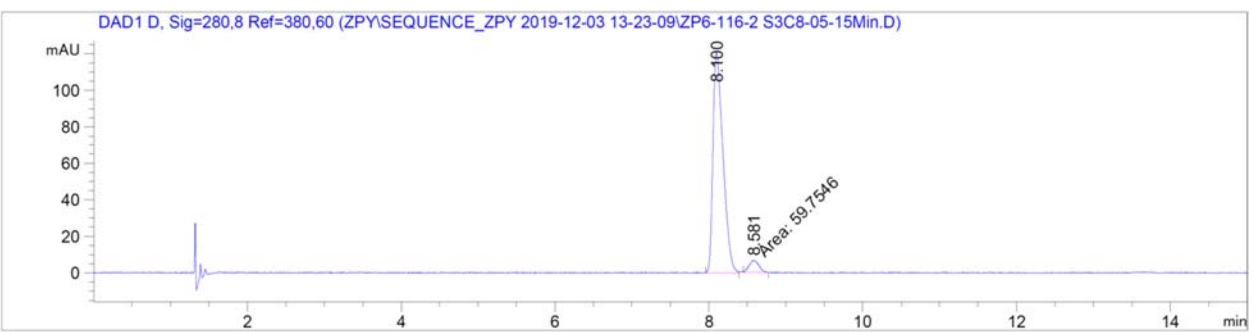


Figure 2B, entry 12

(*S*,*S*)–**L1**: 90% ee
(*R*,*R*)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.171	MM	0.1237	107.88940	14.53316	5.1492
2	8.482	MM	0.1763	1987.38599	187.82870	94.8508



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.100	BB	0.1369	1093.34375	120.45868	94.8179
2	8.581	MM	0.1516	59.75459	6.56953	5.1821

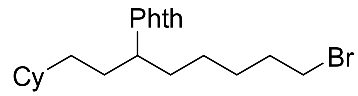
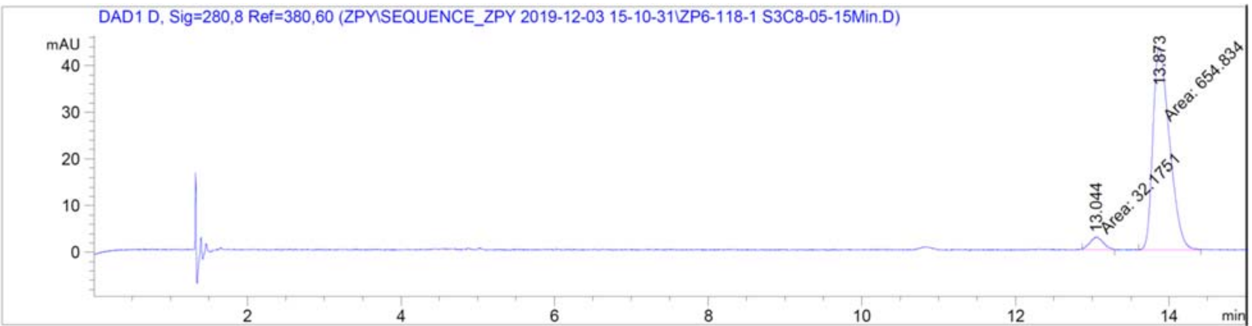
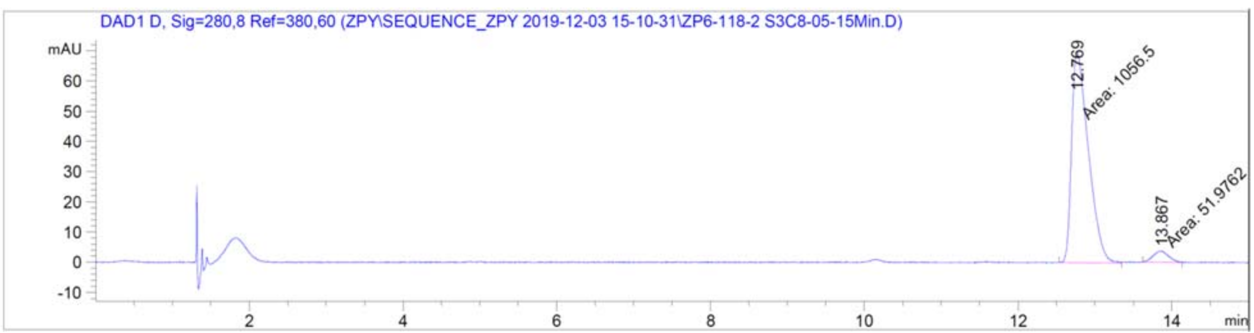


Figure 2B, entry 13

(*S*,*S*)–**L1**: 91% ee
(*R*,*R*)–**L1**: 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.044	MM	0.2008	32.17513	2.67089	4.6834
2	13.873	MM	0.2509	654.83374	43.50373	95.3166



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.769	MM	0.2522	1056.50037	69.82286	95.3110
2	13.867	MM	0.2326	51.97620	3.72501	4.6890

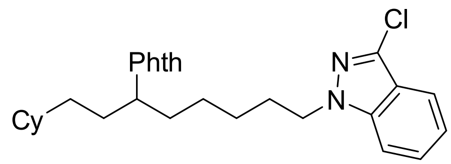
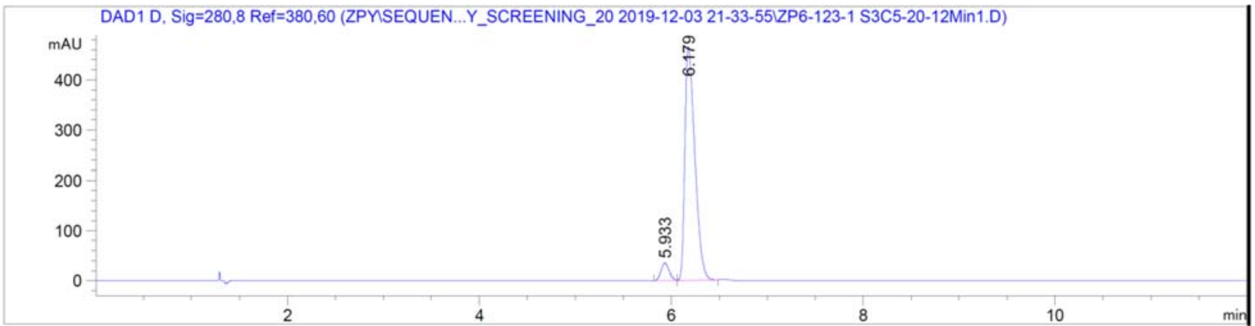
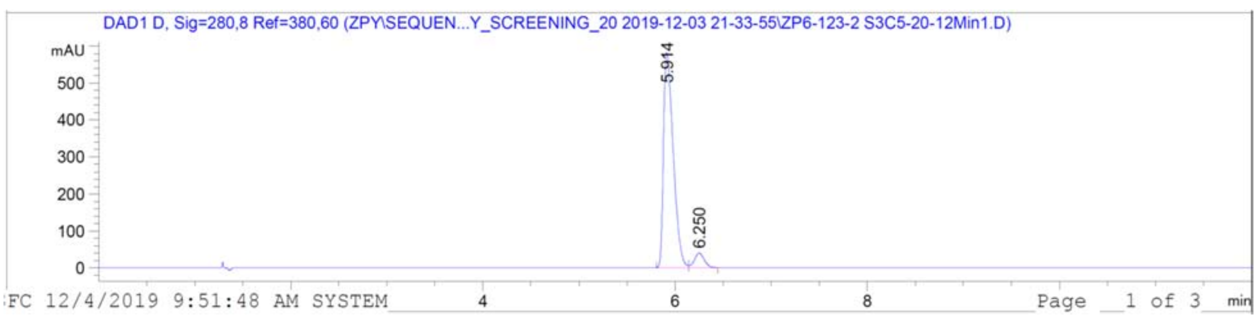


Figure 2B, entry 14

(*S*,*S*)–**L1**: 88% ee
(*R*,*R*)–**L1**: 87% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.933	BV	0.0922	208.37959	35.13285	5.8338
2	6.179	VB	0.1114	3363.55200	464.92273	94.1662



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.914	BV	0.1089	4085.63843	581.96613	93.4174
2	6.250	VB	0.1099	287.89032	40.03067	6.5826

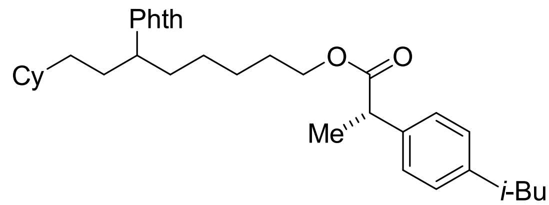
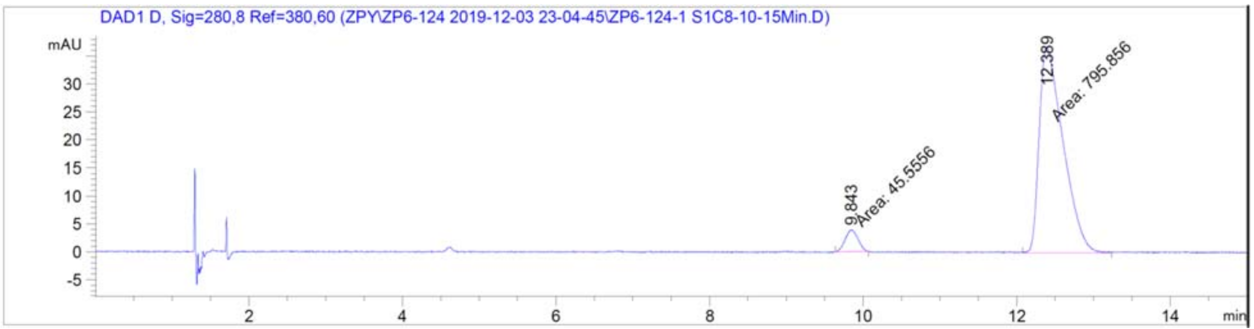
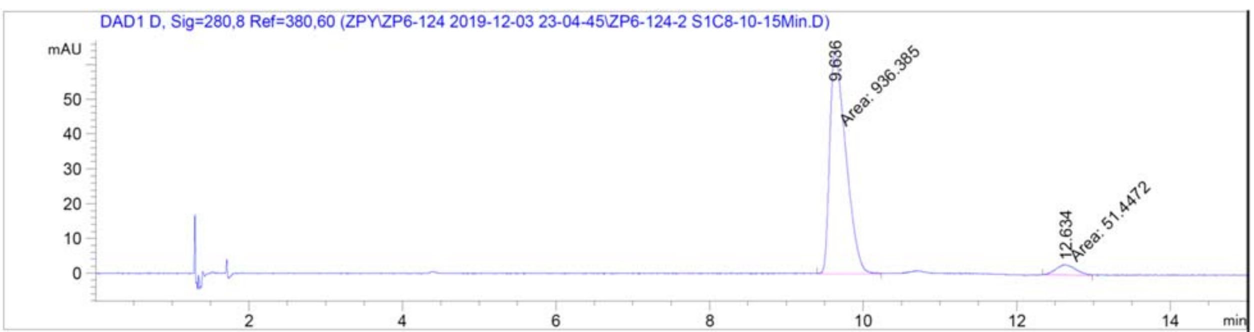


Figure 2B, entries 15 and 16

(*S*,*S*)–**L1**: 95:5 dr
(*R*,*R*)–**L1**: 5:95 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.843	MM	0.1937	45.55561	3.91930	5.4142
2	12.389	MM	0.3606	795.85626	36.77891	94.5858



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.636	MM	0.2445	936.38531	63.83318	94.7919
2	12.634	MM	0.2934	51.44722	2.92265	5.2081

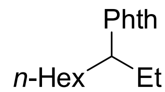
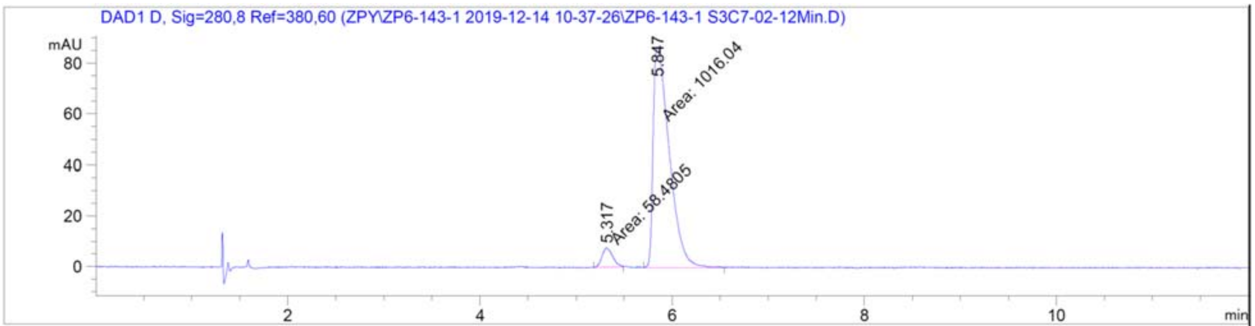
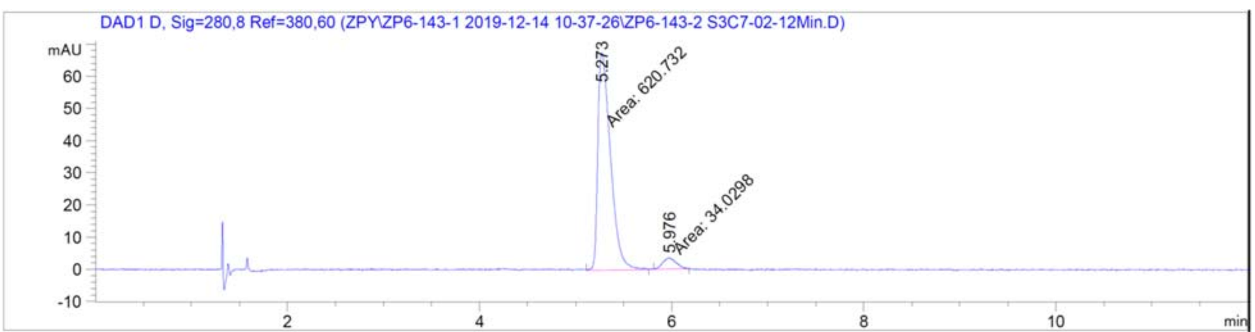


Figure 2B, entry 17

(*S*,*S*)–**L1**: 89% ee
(*R*,*R*)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.317	MM	0.1270	58.48048	7.67385	5.4425
2	5.847	MM	0.1949	1016.04388	86.87975	94.5575



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.273	MM	0.1530	620.73224	67.62050	94.8027
2	5.976	MM	0.1629	34.02985	3.48194	5.1973

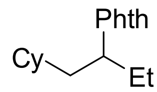
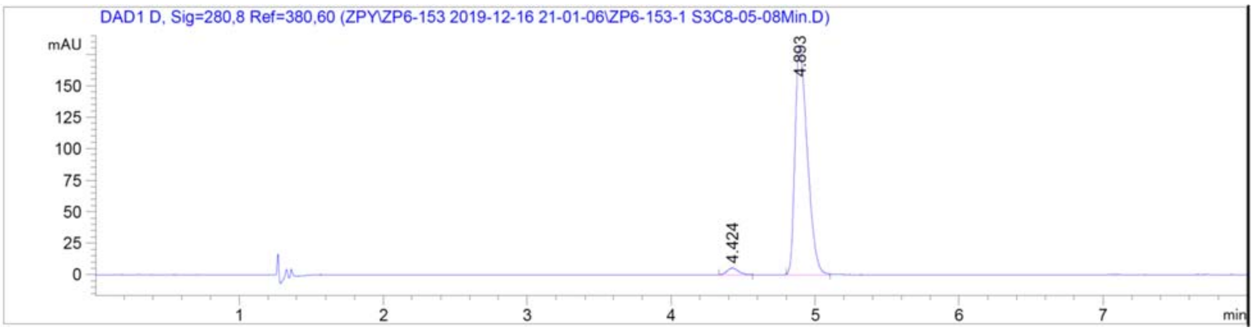
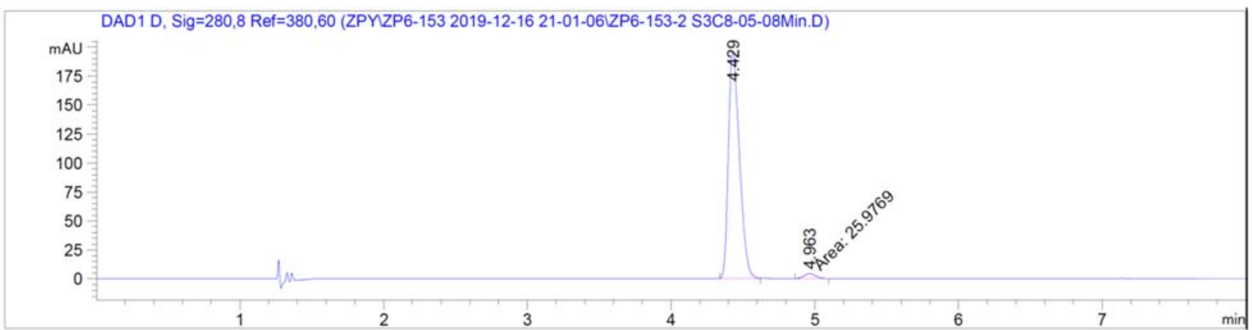


Figure 2B, entry 18

(S,S)–**L1**: 95% ee
(R,R)–**L1**: 95% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.424	BB	0.0804	29.35479	5.39853	2.6525
2	4.893	BB	0.0906	1077.33484	180.71046	97.3475



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.429	BB	0.0837	1053.32800	195.94173	97.5932
2	4.963	MM	0.0949	25.97688	4.55985	2.4068

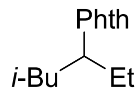
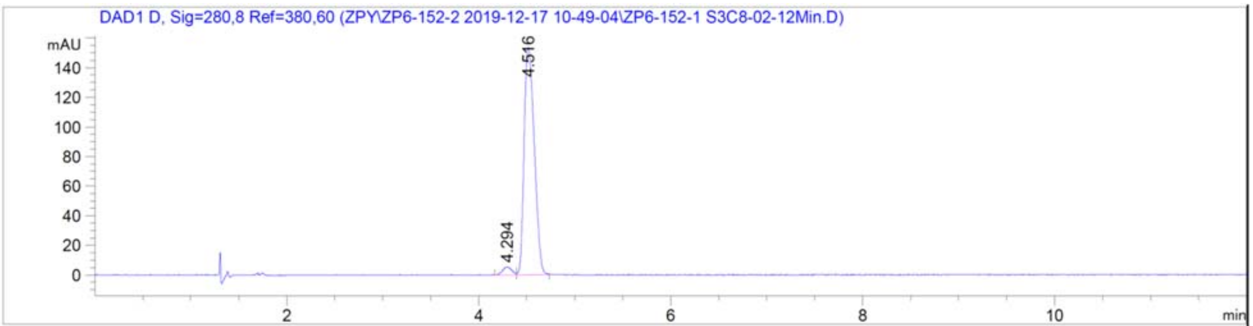
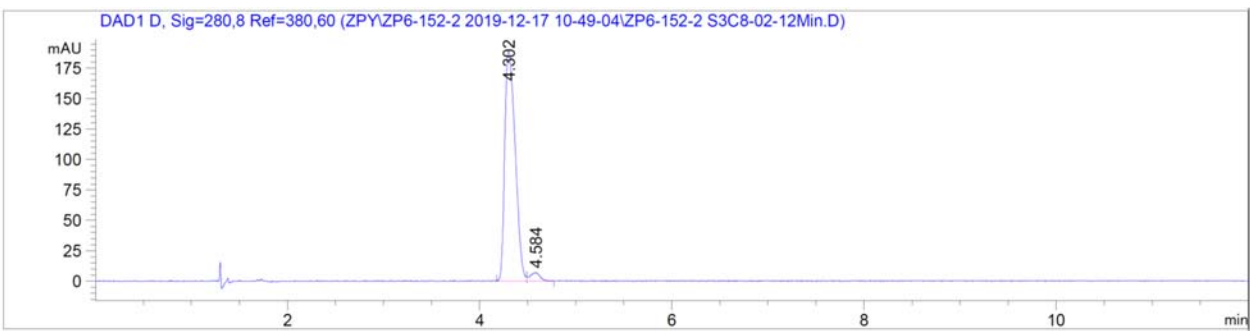


Figure 2B, entry 19

(*S*,*S*)–**L1**: 94% ee
(*R*,*R*)–**L1**: 93% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.294	BV	0.0890	34.76719	5.26670	2.9815
2	4.516	VB	0.1190	1131.34290	153.53853	97.0185



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.302	BV	0.1213	1430.11731	188.93886	96.6347
2	4.584	VB	0.0985	49.80413	6.87862	3.3653

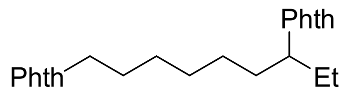
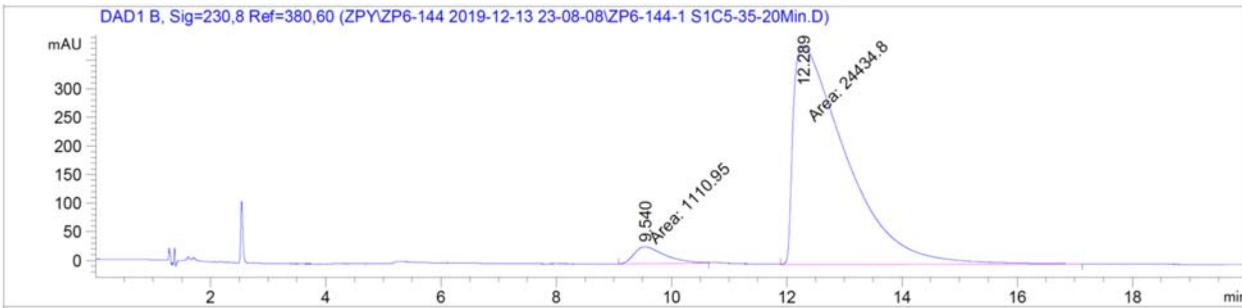
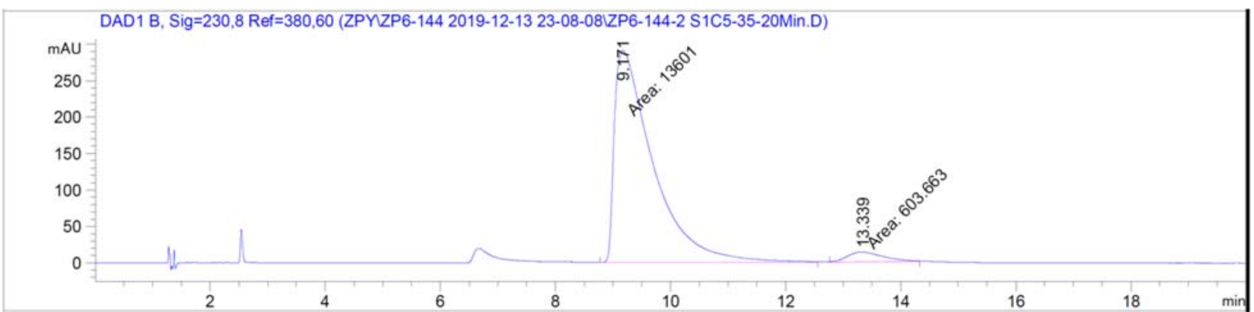


Figure 2B, entry 20

(*S*,*S*)–**L1**: 91% ee
(*R*,*R*)–**L1**: 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.540	MM	0.6281	1110.95410	29.47913	4.3489
2	12.289	MM	1.0659	2.44348e4	382.05591	95.6511



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.171	MM	0.7784	1.36010e4	291.20837	95.7502
2	13.339	MM	0.7289	603.66290	13.80230	4.2498

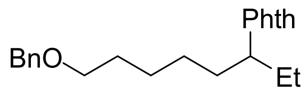
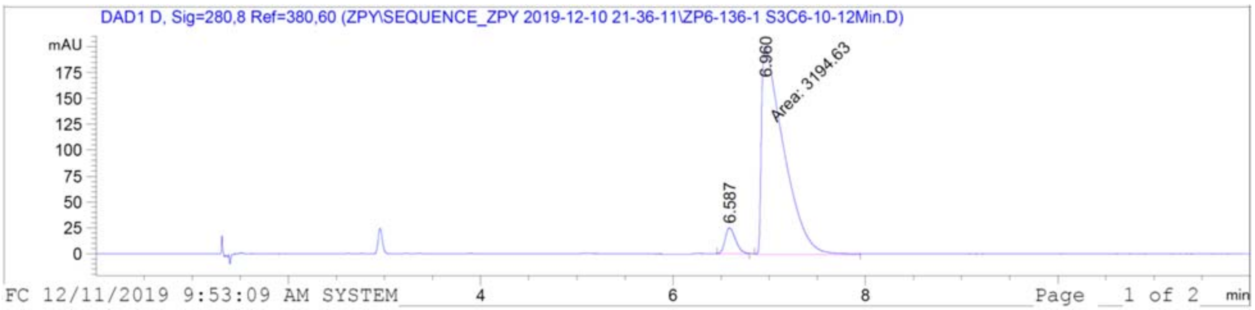
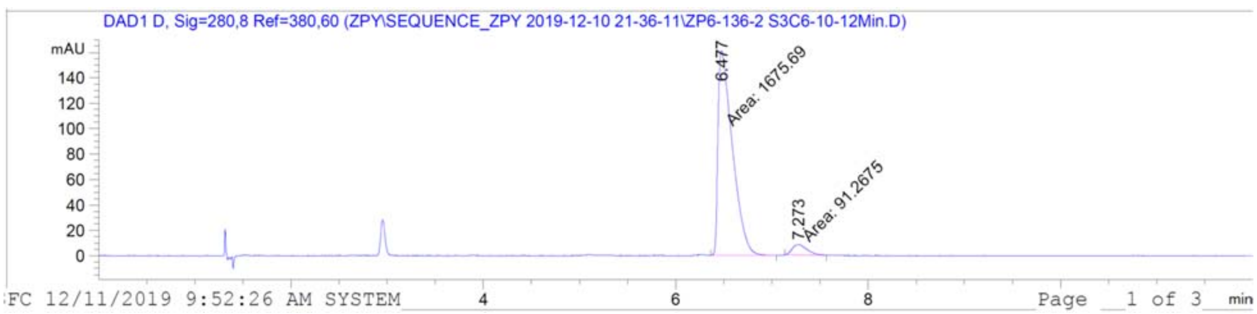


Figure 2B, entry 21

(*S*,*S*)–**L1**: 89% ee
(*R*,*R*)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.587	BB	0.1166	190.19641	25.05763	5.6191
2	6.960	MM	0.2651	3194.62646	200.86368	94.3809



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.477	MM	0.1732	1675.68677	161.25468	94.8348
2	7.273	MM	0.1812	91.26749	8.39300	5.1652

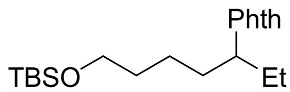
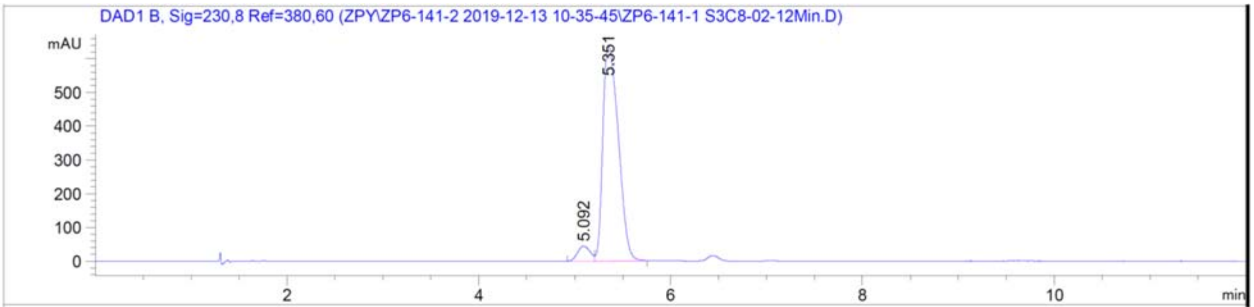
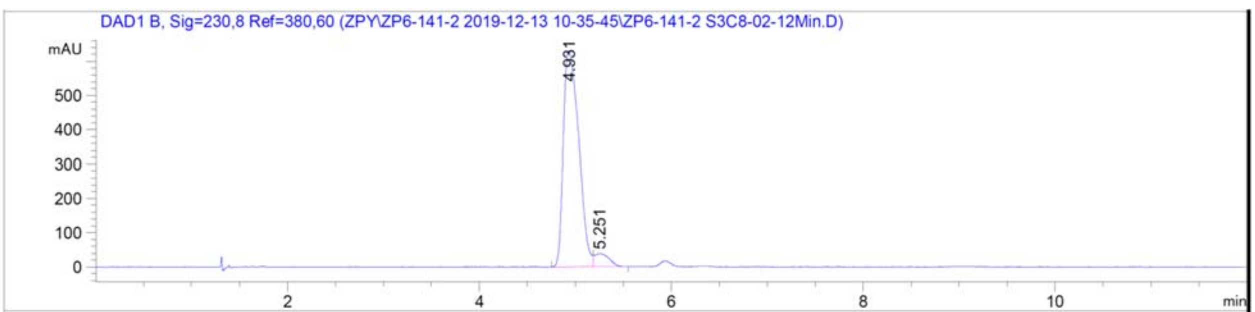


Figure 2B, entry 22

(*S*,*S*)–**L1**: 89% ee
(*R*,*R*)–**L1**: 89% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.092	BV	0.1271	404.14886	44.44057	5.3368
2	5.351	VB	0.1820	7168.66846	638.67108	94.6632



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.931	BV	0.1834	7042.97607	630.28583	94.3799
2	5.251	VB	0.1399	419.39569	37.95276	5.6201

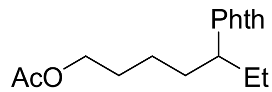
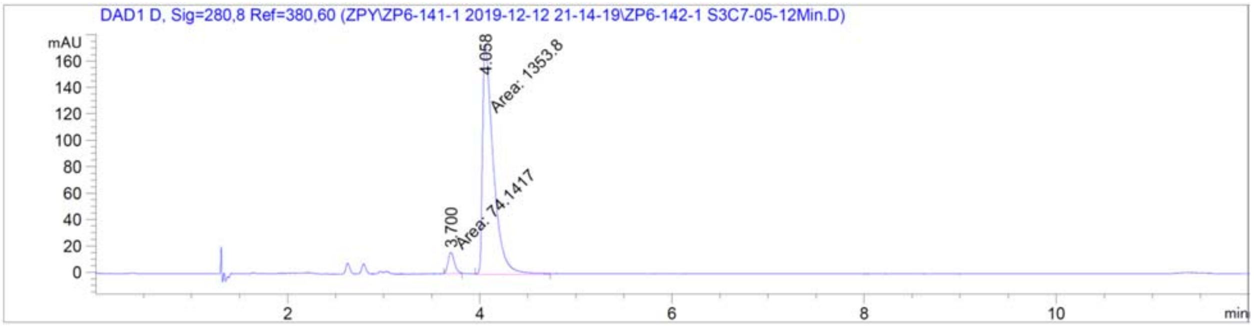
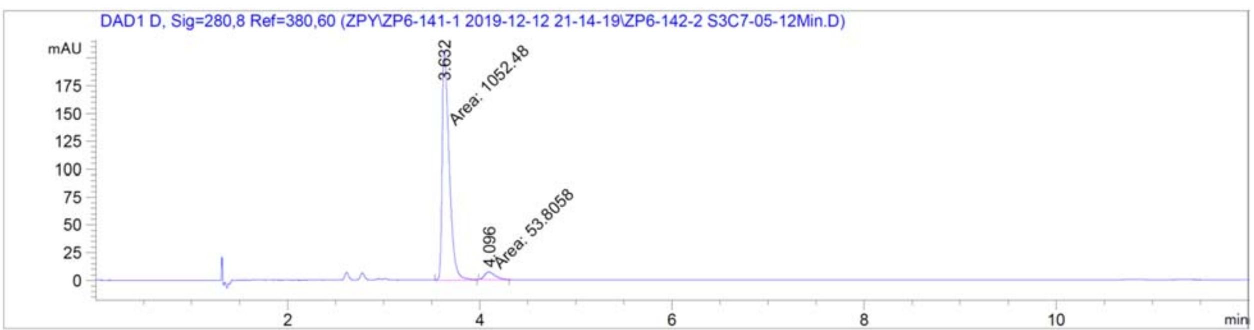


Figure 2B, entry 23

(*S*,*S*)–**L1**: 90% ee
(*R*,*R*)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.700	MM	0.0762	74.14165	16.20678	5.1922
2	4.058	MM	0.1302	1353.79980	173.24287	94.8078



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.632	MM	0.0850	1052.48438	206.30443	95.1364
2	4.096	MM	0.1282	53.80582	6.99542	4.8636

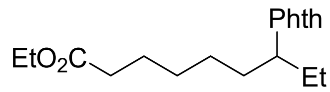
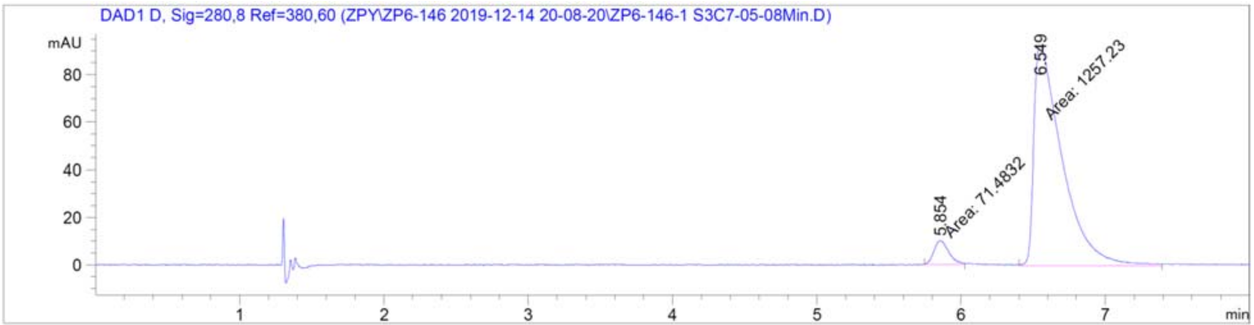
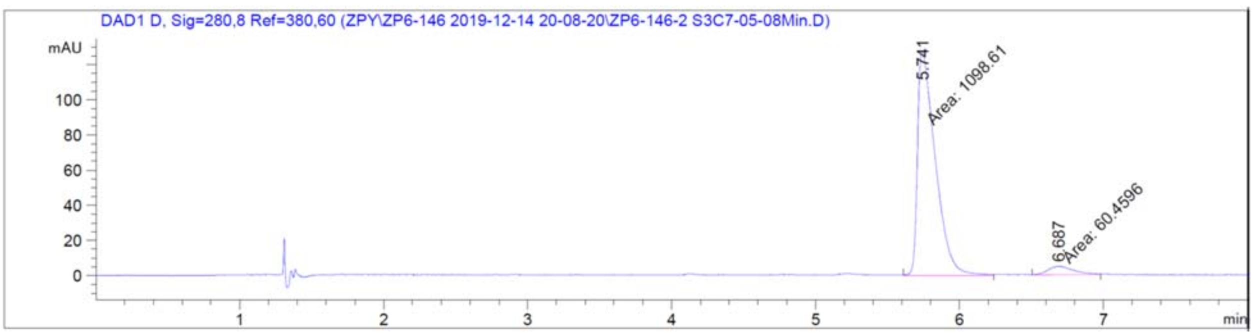


Figure 2B, entry 24

(*S*,*S*)–**L1**: 89% ee
(*R*,*R*)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.854	MM	0.1184	71.48318	10.06209	5.3799
2	6.549	MM	0.2267	1257.22974	92.42210	94.6201



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.741	MM	0.1431	1098.60742	127.91978	94.7838
2	6.687	MM	0.2098	60.45962	4.80408	5.2162

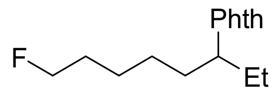
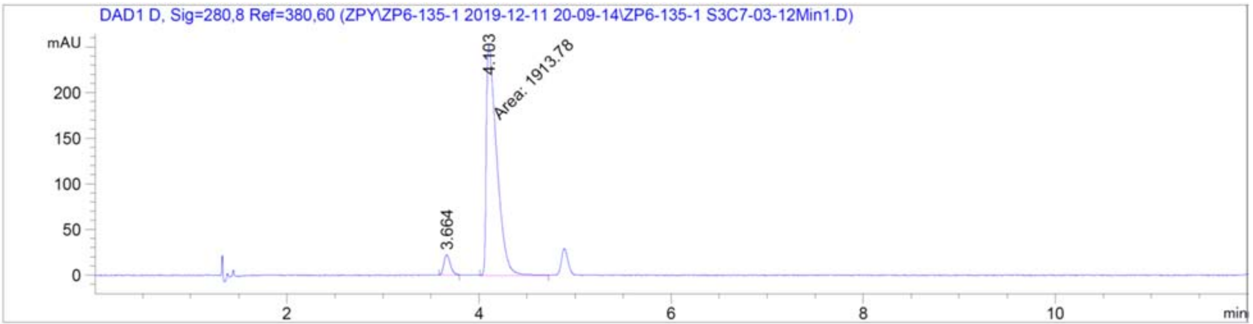
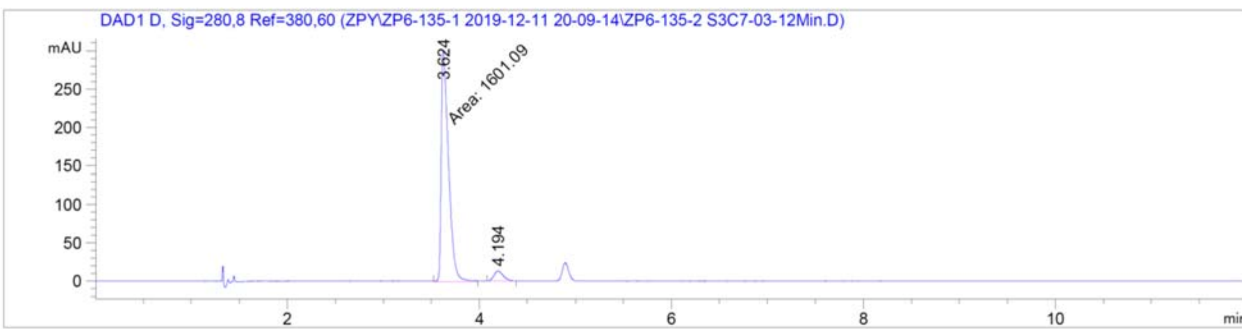


Figure 2B, entry 25

(*S*,*S*)–**L1**: 90% ee
(*R*,*R*)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.664	BB	0.0737	105.95458	22.17718	5.2460
2	4.103	MM	0.1265	1913.77637	252.09315	94.7540



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.624	MM	0.0885	1601.09216	301.42300	94.8227
2	4.194	BB	0.0980	87.41895	13.08110	5.1773

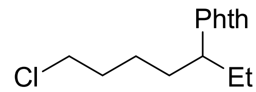
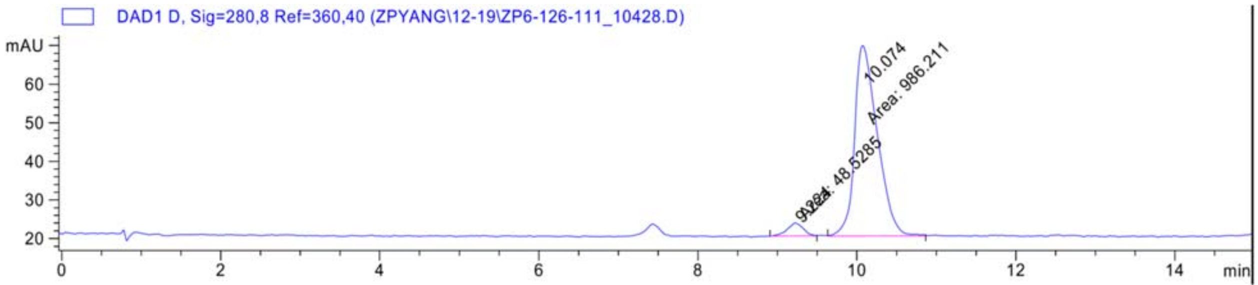
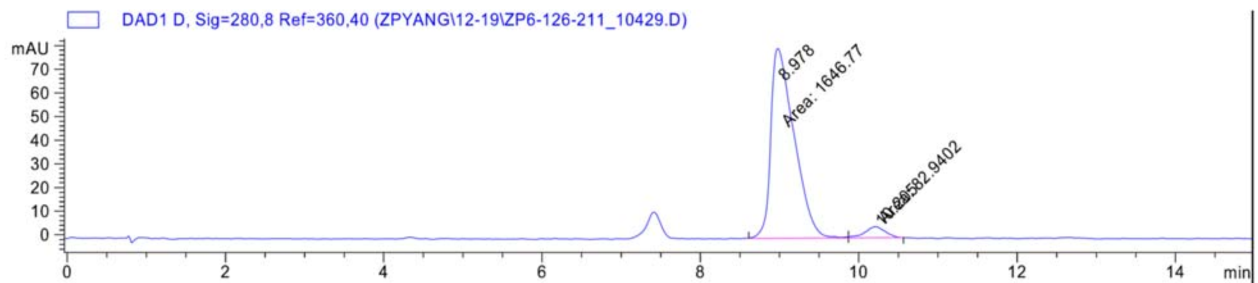


Figure 2B, entry 26

(*S*,*S*)–**L1**: 91% ee
(*R*,*R*)–**L1**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.224	MM	0.2370	48.52854	3.41252	4.6899
2	10.074	MM	0.3324	986.21057	49.45481	95.3101



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.978	MF	0.3419	1646.76721	80.28491	95.2050
2	10.205	FM	0.2956	82.94022	4.67618	4.7950

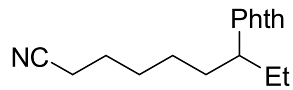
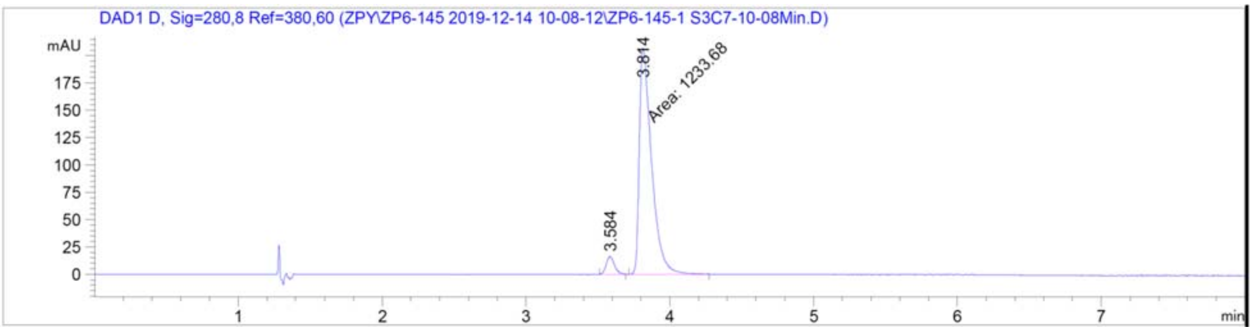
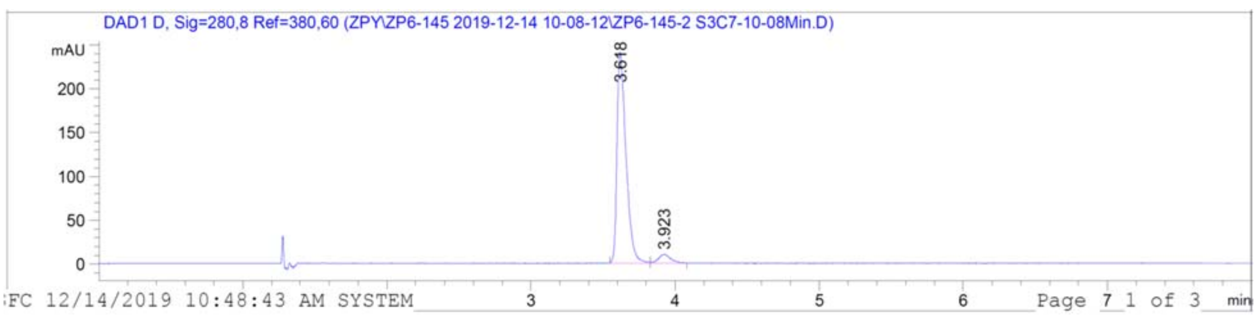


Figure 2B, entry 27

(*S*,*S*)–**L1**: 90% ee
(*R*,*R*)–**L1**: 89% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.584	BB	0.0603	65.24456	16.44624	5.0230
2	3.814	MM	0.0993	1233.68066	207.11505	94.9770



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.618	BB	0.0658	1049.81580	240.96671	94.5625
2	3.923	BB	0.0879	60.36629	9.93794	5.4375

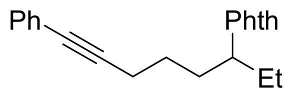
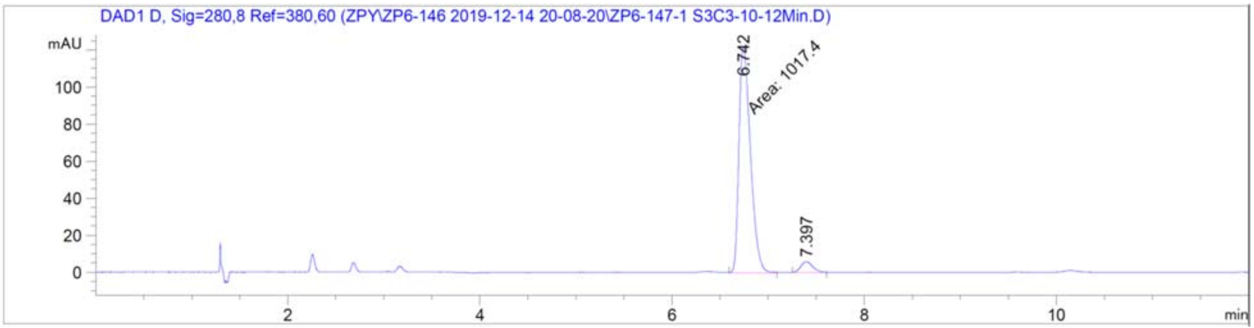
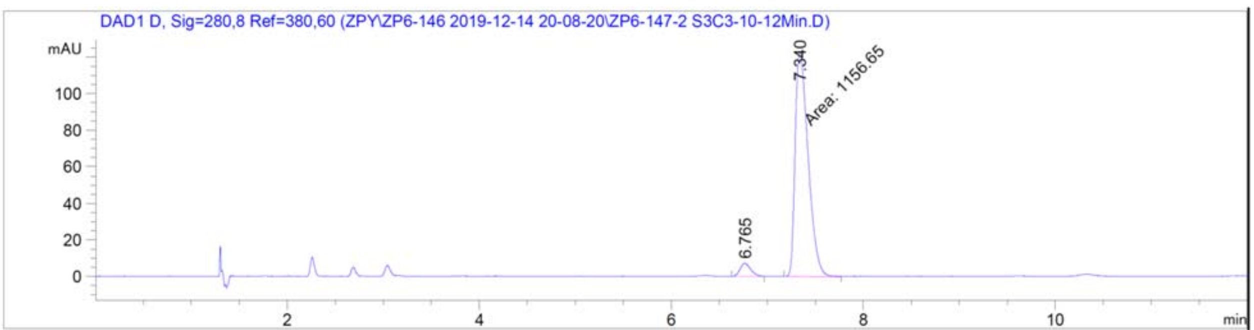


Figure 2B, entry 28

(*S*,*S*)–**L1**: 91% ee
(*R*,*R*)–**L1**: 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.742	MM	0.1387	1017.39825	122.25273	95.3876
2	7.397	BB	0.1157	49.19613	5.75671	4.6124



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.765	BB	0.1141	55.20236	7.06852	4.5552
2	7.340	MM	0.1565	1156.65051	123.19755	95.4448

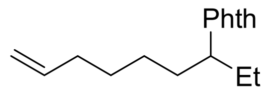
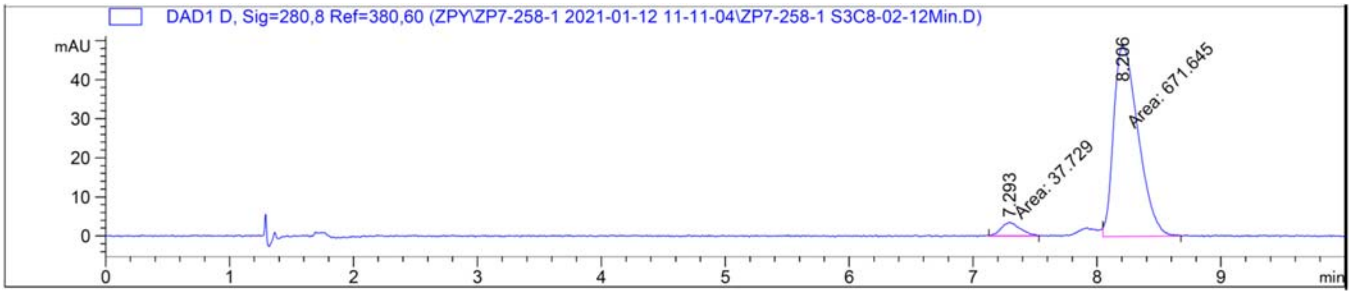
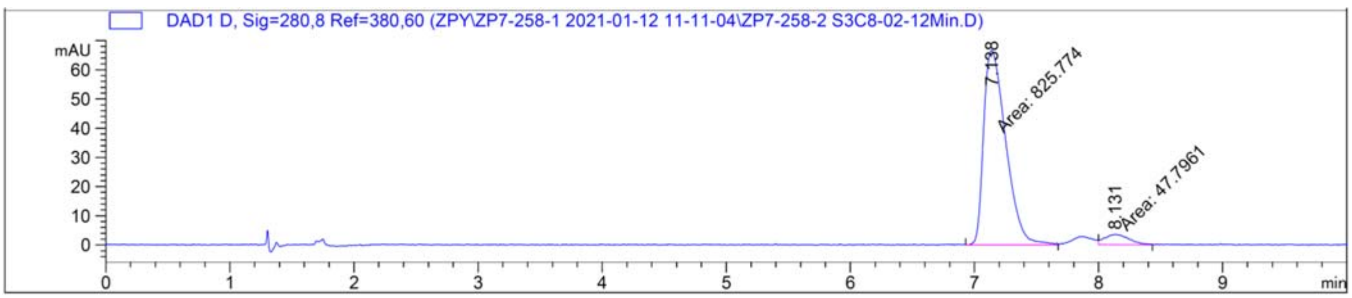


Figure 2B, entry 29

(*S*,*S*)–**L1**: 89% ee
(*R*,*R*)–**L1**: 89% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.293	MM	0.1800	37.72897	3.49289	5.3186
2	8.206	MM	0.2300	671.64502	48.66127	94.6814



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.138	MM	0.2068	825.77399	66.55161	94.5286
2	8.131	MM	0.2293	47.79609	3.47466	5.4714

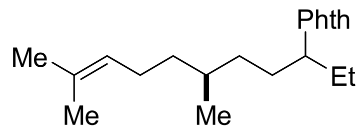
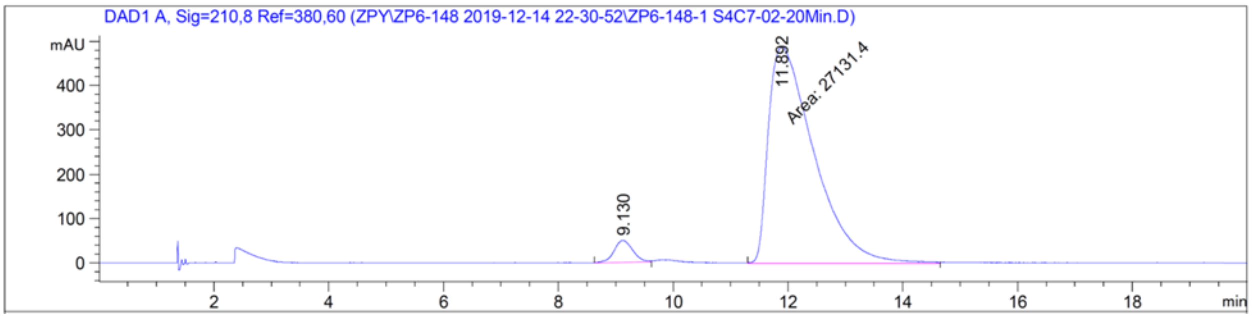
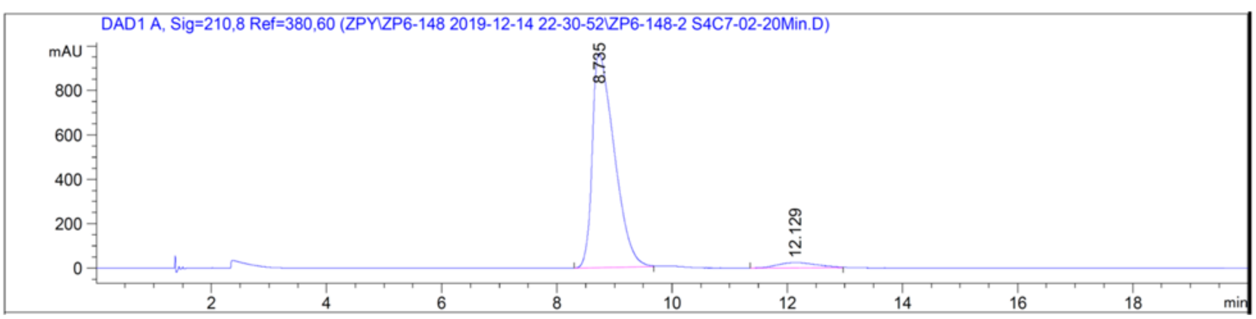


Figure 2B, entries 30 and 31

(S,S)–**L1**: 96:4 dr
(R,R)–**L1**: 4:96 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.130	BV	0.2699	1128.85559	49.72022	3.9945
2	11.892	MM	0.9236	2.71314e4	489.59491	96.0055



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.735	BB	0.3670	2.56204e4	964.34283	95.9131
2	12.129	BB	0.5471	1091.68506	23.58030	4.0869

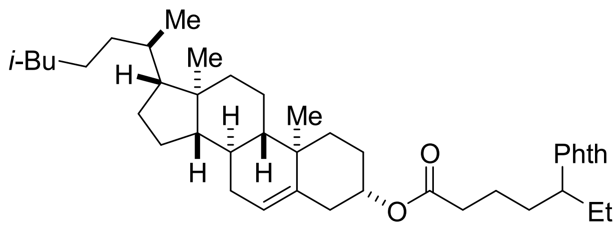
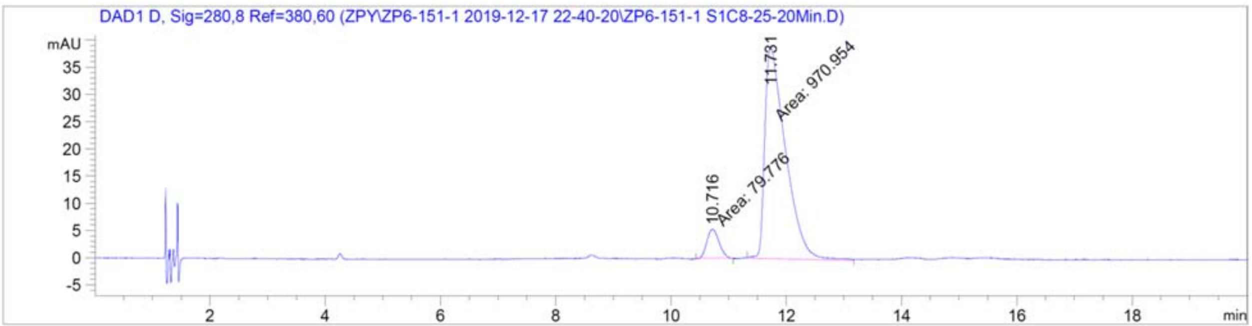
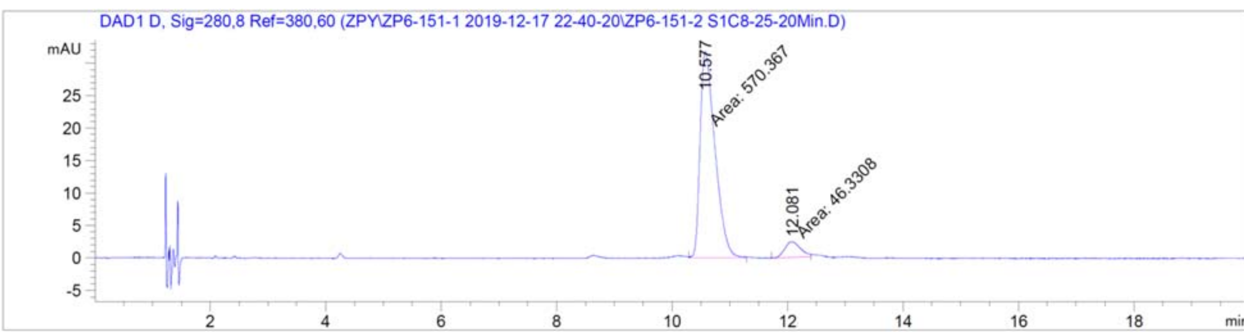


Figure 2B, entries 32 and 33

(S,S)–**L1**: 92:8 dr
(R,R)–**L1**: 8:92 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.716	MM	0.2476	79.77602	5.37087	7.5924
2	11.731	MM	0.4152	970.95441	38.97978	92.4076



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.577	MM	0.2993	570.36713	31.76212	92.4873
2	12.081	MM	0.3177	46.33077	2.43079	7.5127

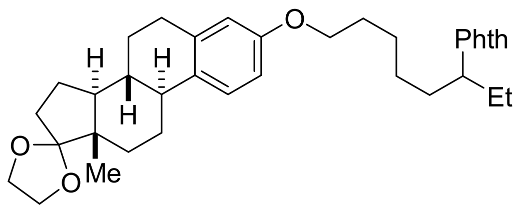
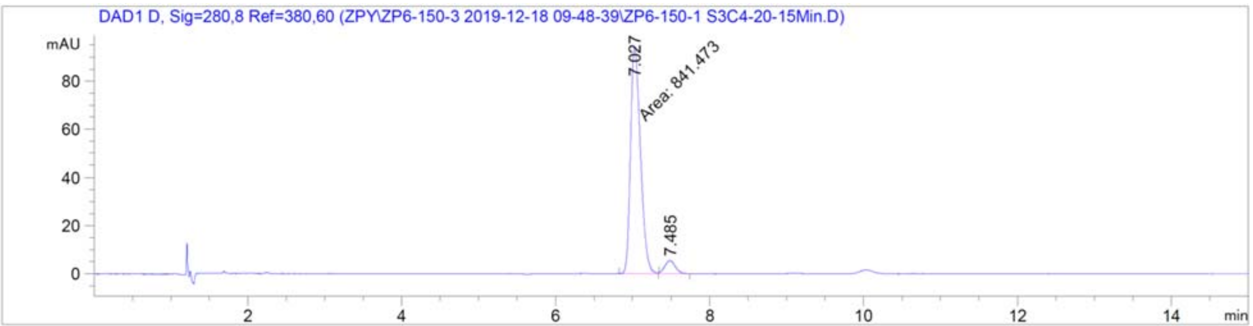
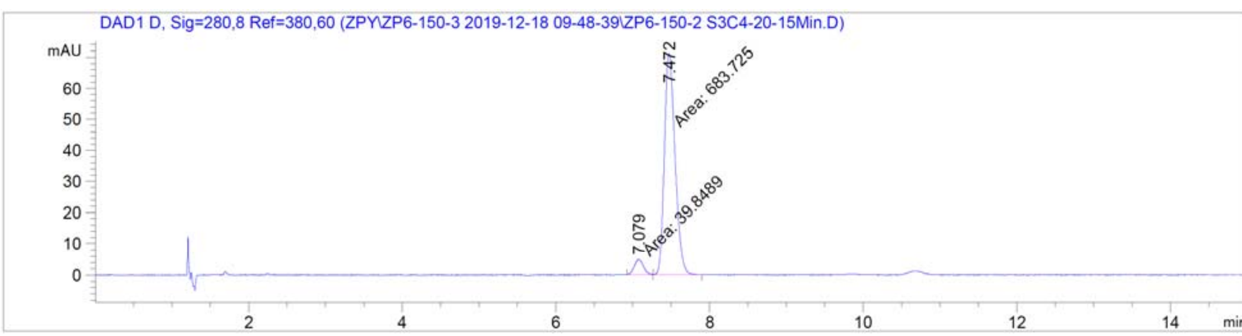


Figure 2B, entries 34 and 35

(*S*,*S*)–**L1**: 94:6 dr
(*R*,*R*)–**L1**: 6:94 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.027	MM	0.1489	841.47314	94.21201	94.1744
2	7.485	BB	0.1488	52.05298	5.48153	5.8256



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.079	MM	0.1376	39.84894	4.82533	5.5072
2	7.472	MM	0.1601	683.72534	71.16126	94.4928

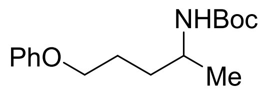
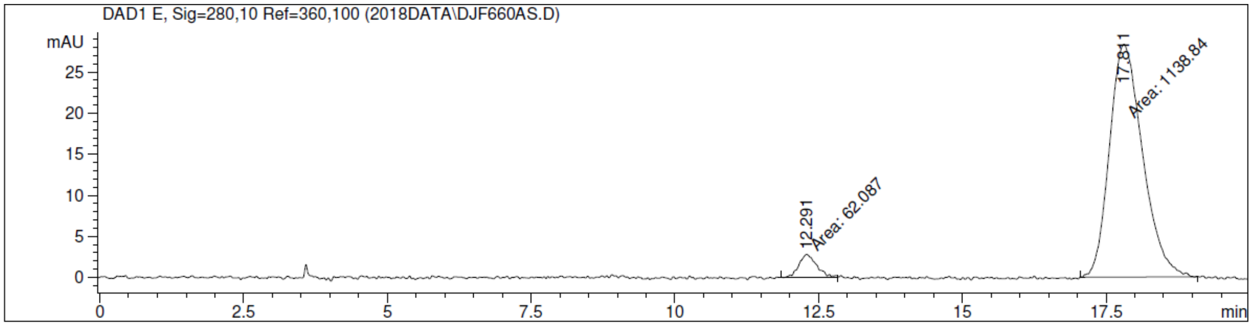
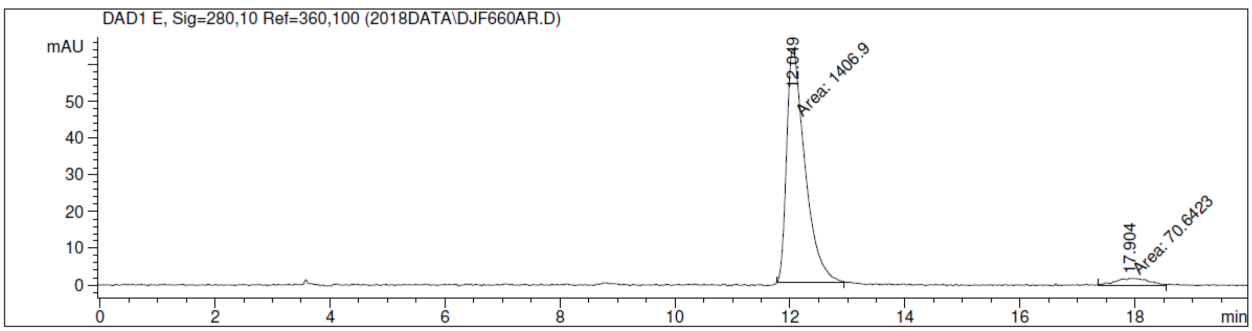


Figure 4B, entry 36

(*S*,*S*)–**L2**: 90% ee
(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.291	MM	0.3656	62.08702	2.83070	5.1699
2	17.811	MM	0.6691	1138.83704	28.36659	94.8301



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.049	MM	0.3688	1406.90271	63.58581	95.2189
2	17.904	MM	0.6480	70.64226	1.81690	4.7811

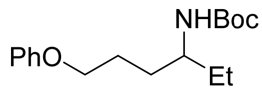
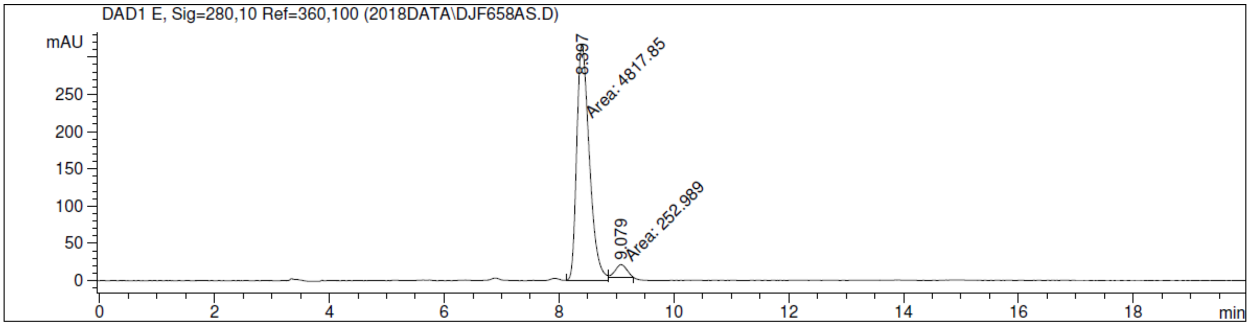
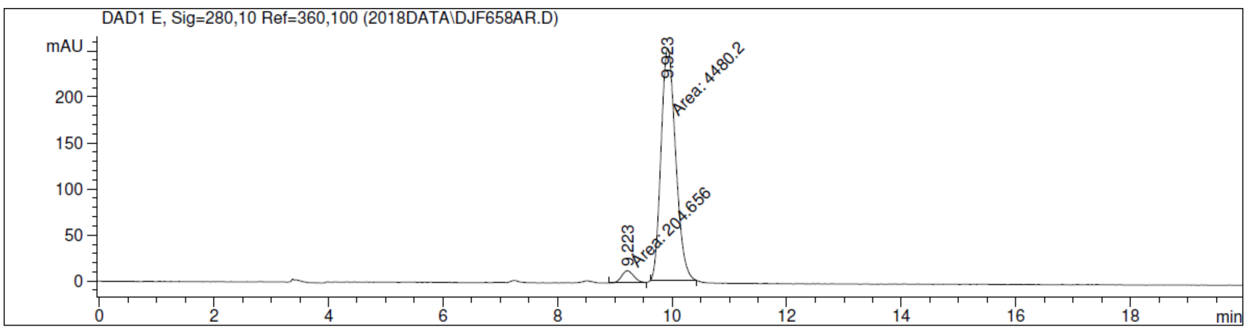


Figure 4B, entry 37

(*S*,*S*)–**L2**: 90% ee
(*R*,*R*)–**L2**: 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.397	MM	0.2539	4817.85498	316.25742	95.0109
2	9.079	MM	0.2397	252.98851	17.59271	4.9891



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.223	MM	0.2539	204.65591	13.43624	4.3685
2	9.923	MM	0.2963	4480.19531	252.01784	95.6315

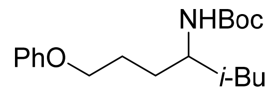
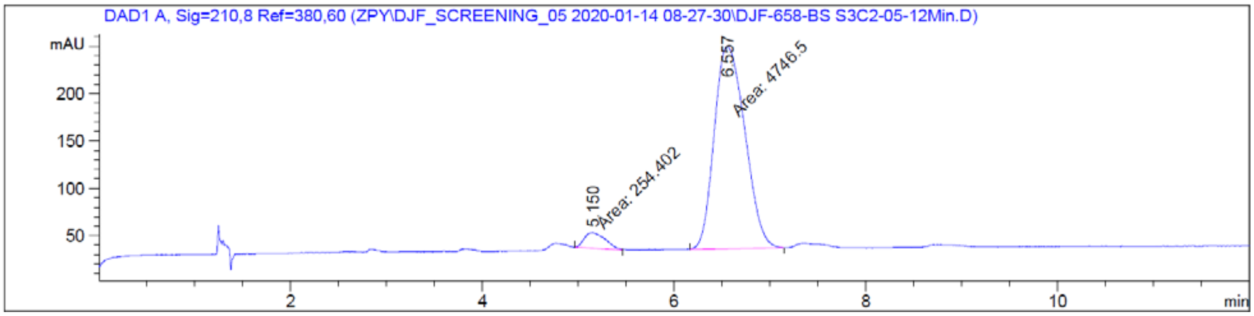
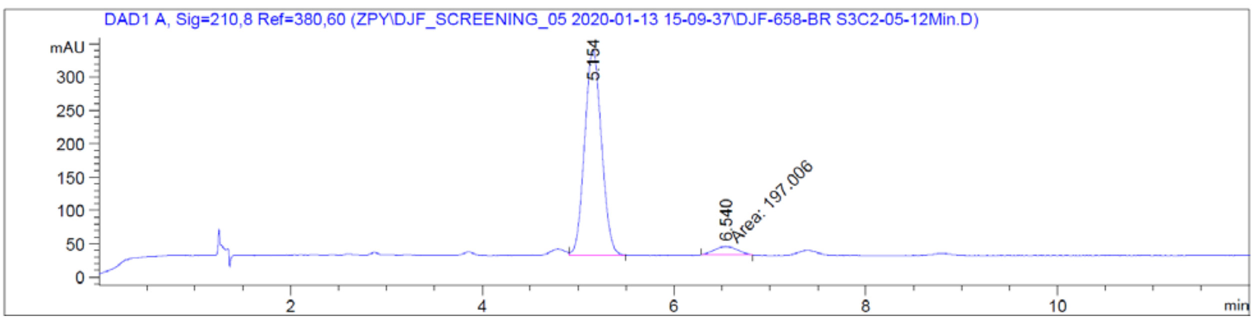


Figure 4B, entry 38

(*S*,*S*)–**L2**: 90% ee
(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.150	MM	0.2574	254.40204	16.47324	5.0871
2	6.557	MM	0.3697	4746.50000	213.98251	94.9129



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.154	VB	0.1906	3766.38745	308.08981	95.0294
2	6.540	MM	0.2648	197.00578	12.39960	4.9706

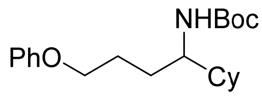
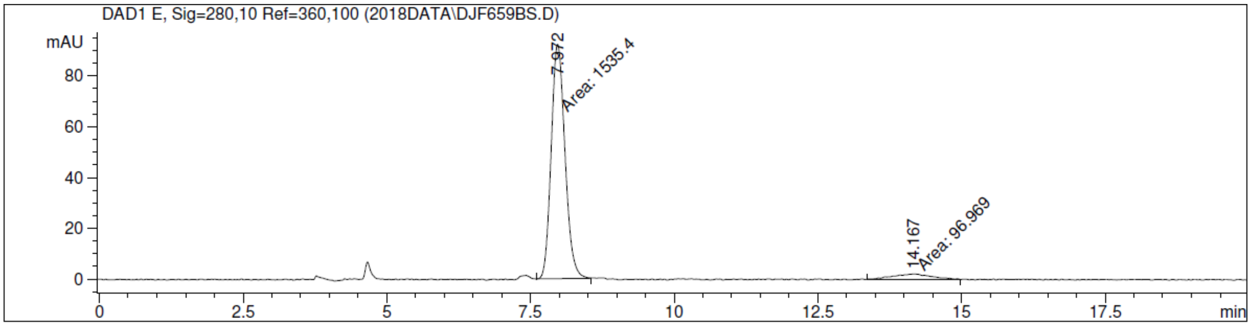
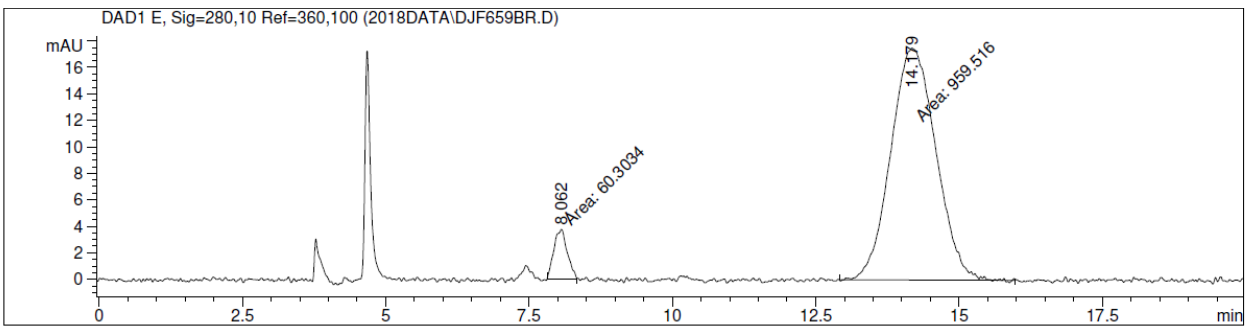


Figure 4B, entry 39

(*S*,*S*)–**L2**: 88% ee
(*R*,*R*)–**L2**: 88% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.972	MM	0.2772	1535.40430	92.31374	94.0596
2	14.167	MM	0.7618	96.96903	2.12158	5.9404



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.062	MM	0.2694	60.30344	3.73126	5.9131
2	14.179	MM	0.9128	959.51599	17.51874	94.0869

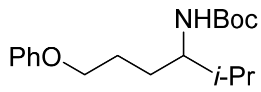
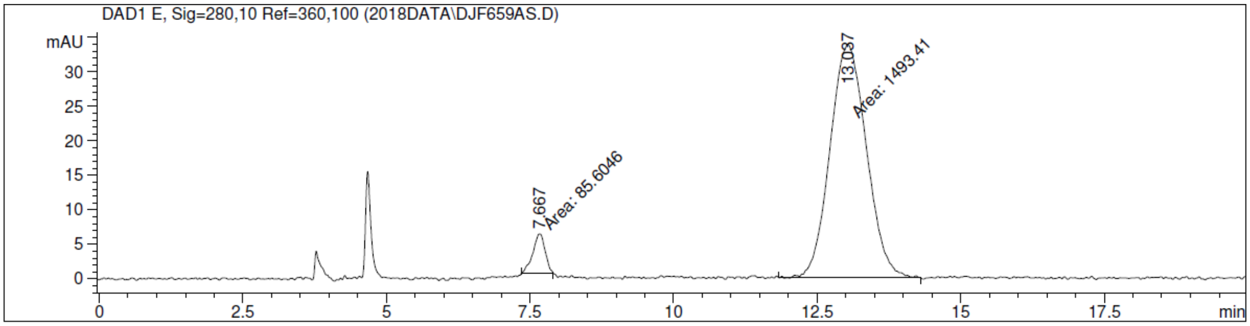
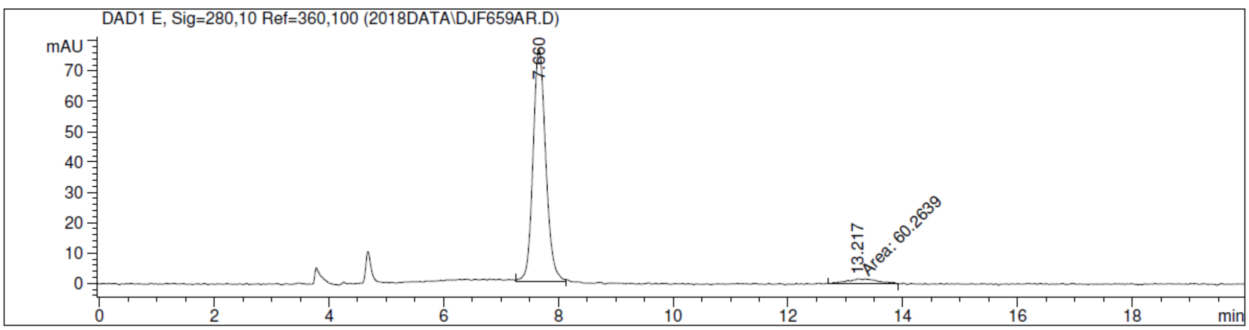


Figure 4B, entry 40

(S,S)–**L2**: 89% ee
(R,R)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.667	MM	0.2485	85.60458	5.74081	5.4214
2	13.037	MM	0.7359	1493.40991	33.82073	94.5786



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.660	BB	0.2382	1184.78723	76.71400	95.1597
2	13.217	MM	0.6136	60.26389	1.63691	4.8403

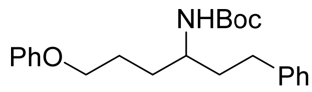
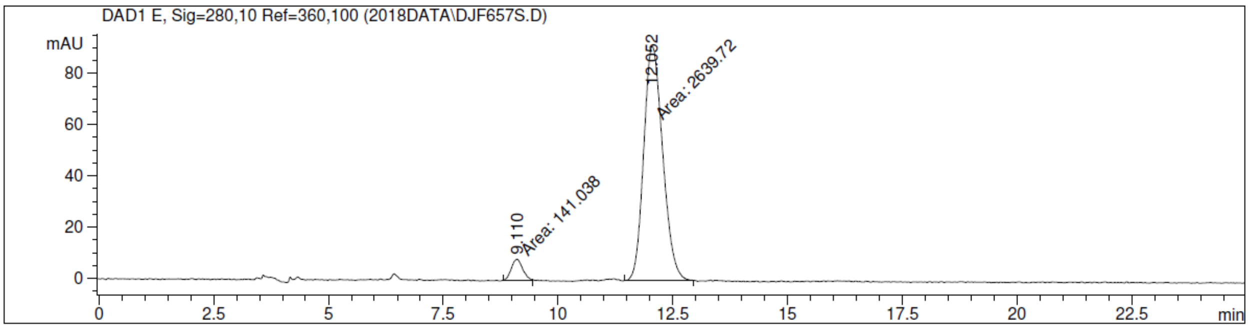
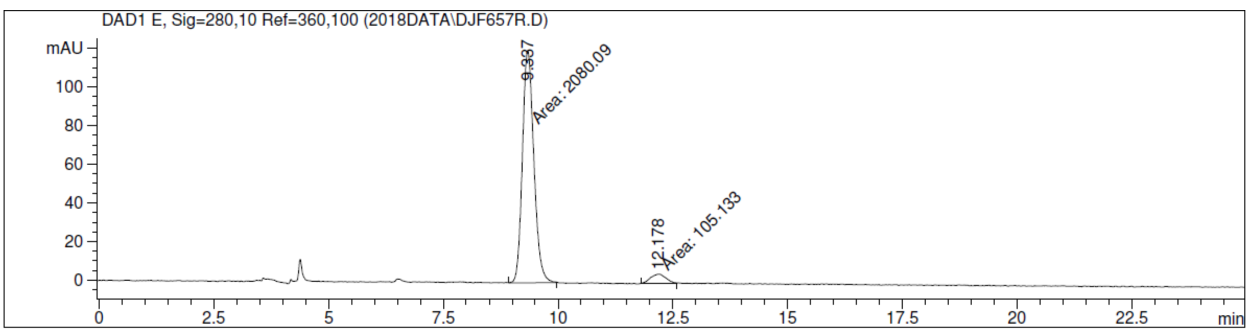


Figure 4B, entry 41

(S,S)–**L2**: 90% ee
(R,R)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.110	MM	0.2866	141.03777	8.20217	5.0719
2	12.052	MM	0.4809	2639.72266	91.48346	94.9281



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.337	MM	0.2886	2080.09424	120.13209	95.1889
2	12.178	MM	0.3811	105.13286	4.59821	4.8111

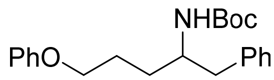
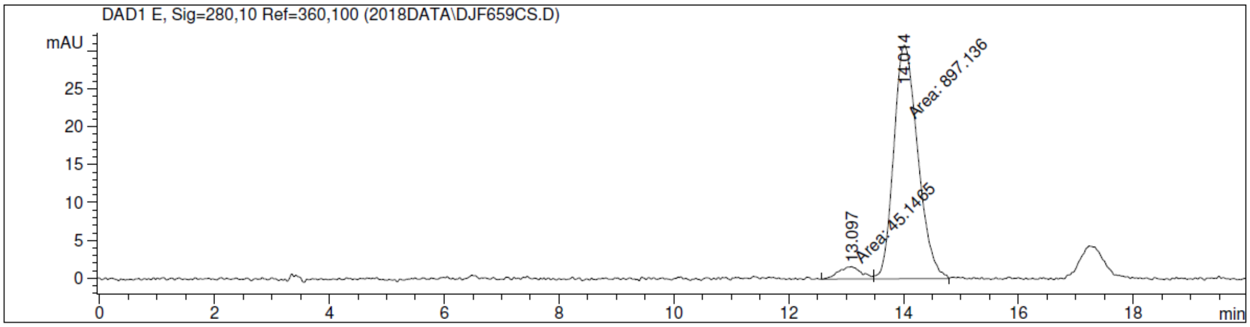
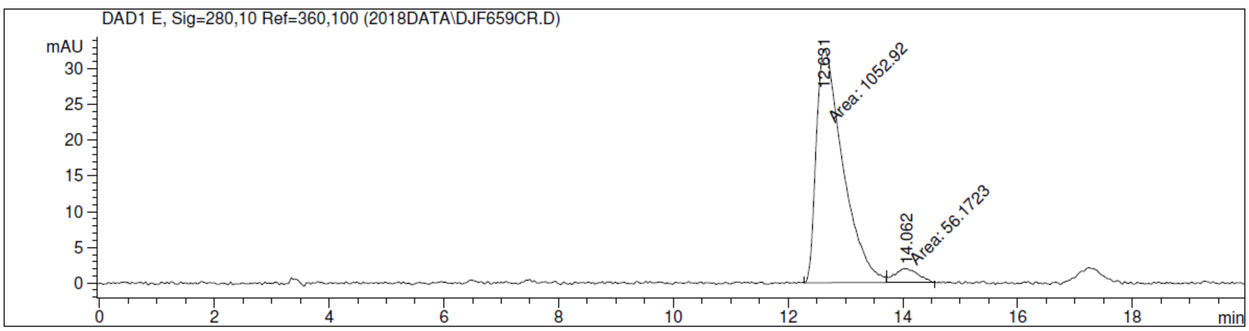


Figure 4B, entry 42

(S,S)–**L2**: 90% ee
(R,R)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.097	MF	0.4617	45.14649	1.62956	4.7912
2	14.014	FM	0.4849	897.13605	30.83659	95.2088



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.631	MF	0.5369	1052.91577	32.68357	94.9353
2	14.062	FM	0.4792	56.17229	1.95376	5.0647

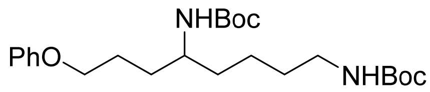
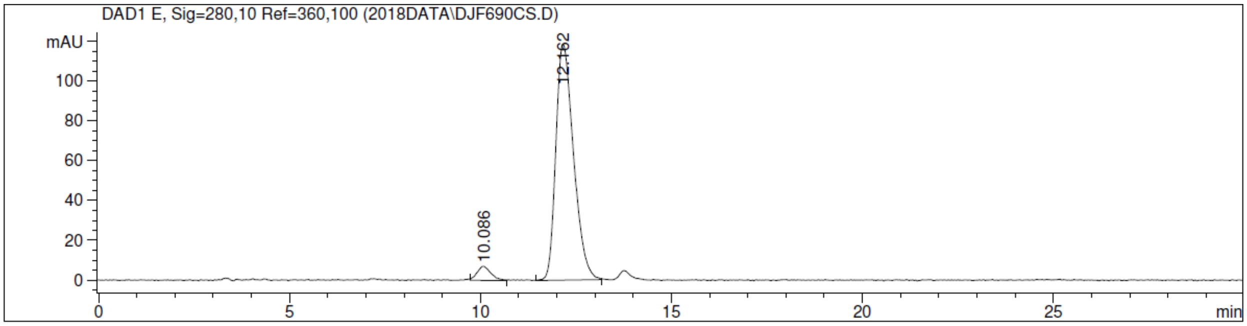
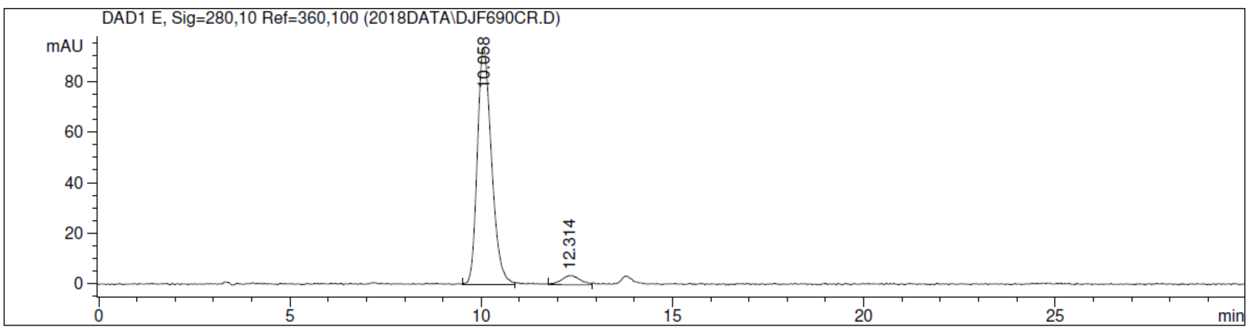


Figure 4B, entry 43

(*S*,*S*)–**L2**: 91% ee
(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.086	VB	0.3294	178.69221	7.05817	4.4616
2	12.162	VB	0.4830	3826.39941	118.39779	95.5384



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.058	BB	0.3895	2425.07812	93.23508	95.1776
2	12.314	VV	0.4056	122.87111	3.66019	4.8224

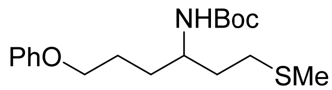
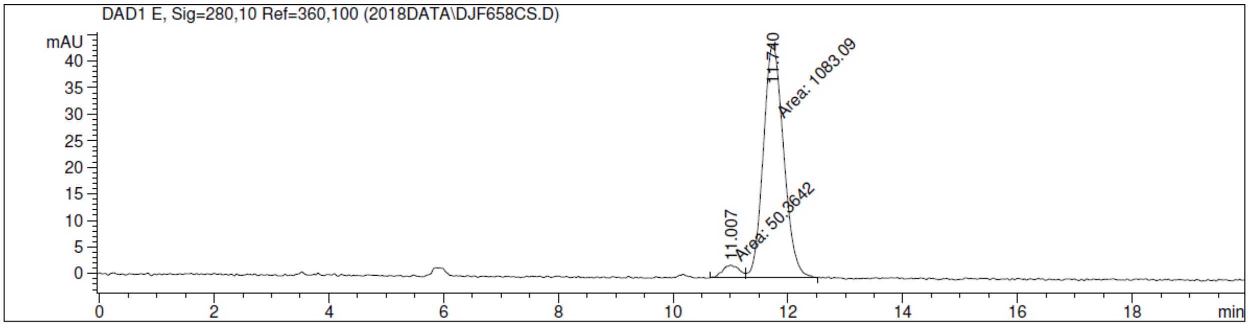
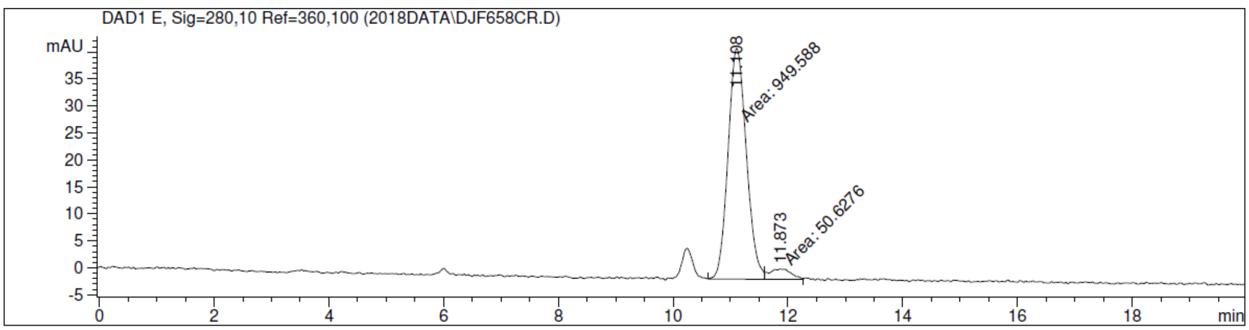


Figure 4B, entry 44

(*S*,*S*)–**L2**: 91% ee
(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.007	MF	0.3479	50.36420	2.41267	4.4434
2	11.740	FM	0.4103	1083.09094	43.99480	95.5566



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.108	MF	0.3698	949.58838	42.79561	94.9383
2	11.873	FM	0.4418	50.62764	1.90975	5.0617

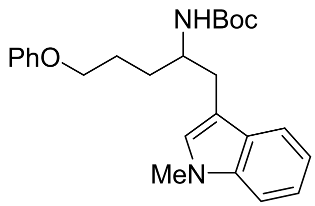
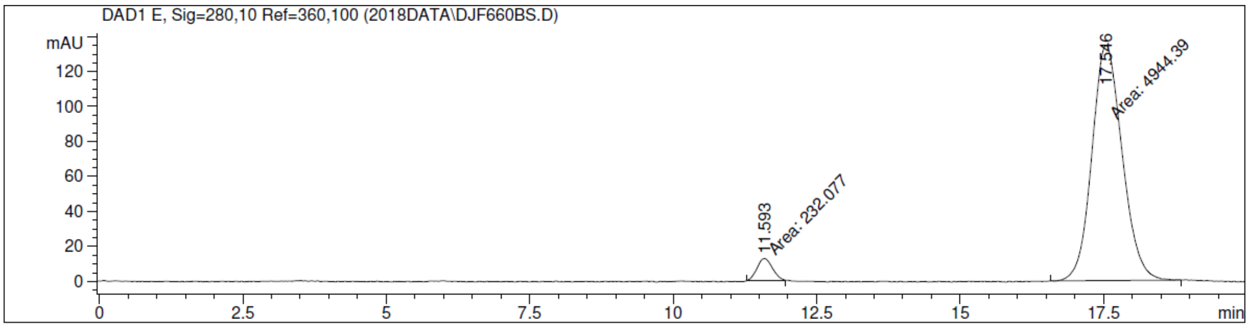
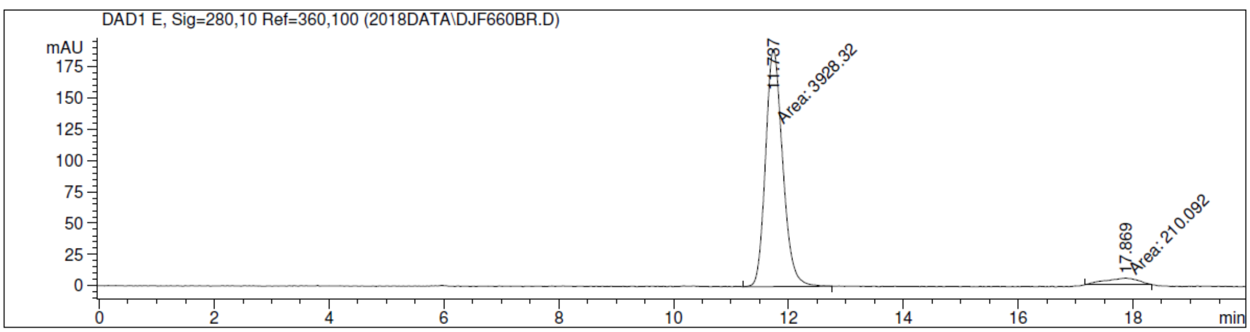


Figure 4B, entry 45

(*S*,*S*)–**L2**: 91% ee
(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.593	MM	0.3090	232.07661	12.51703	4.4833
2	17.546	MM	0.6125	4944.38623	134.55133	95.5167



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.737	MM	0.3463	3928.32300	189.04193	94.9234
2	17.869	MM	0.6780	210.09160	5.16421	5.0766

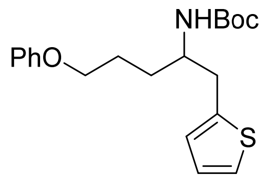
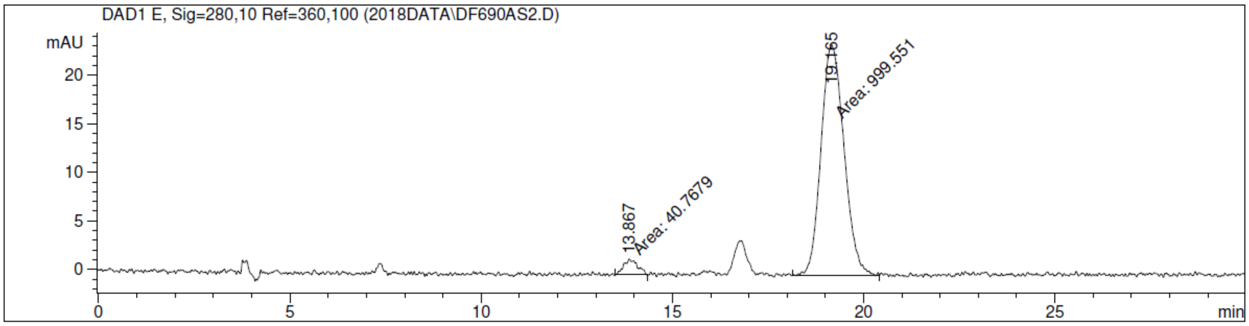
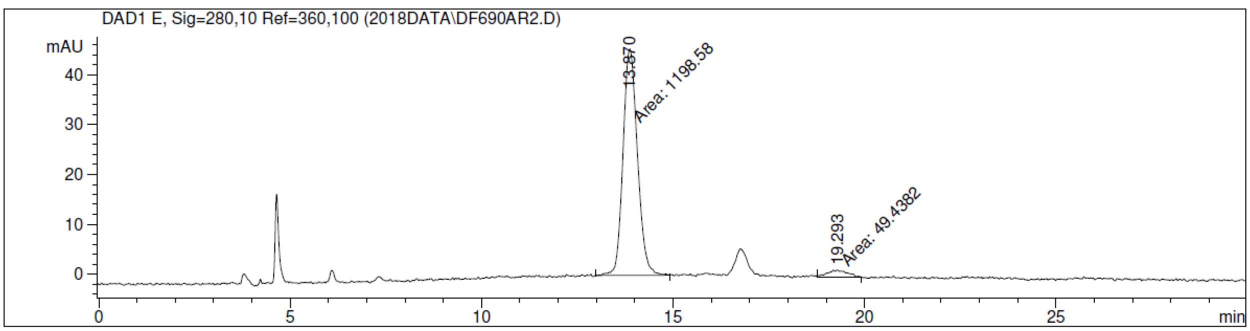


Figure 4B, entry 46

(*S*,*S*)–**L2**: 92% ee
(*R*,*R*)–**L2**: 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.867	MM	0.4157	40.76786	1.63434	3.9188
2	19.165	MM	0.6989	999.55133	23.83659	96.0812



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.870	MM	0.4402	1198.58386	45.38529	96.0387
2	19.293	MM	0.5872	49.43818	1.40330	3.9613

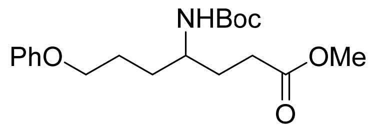
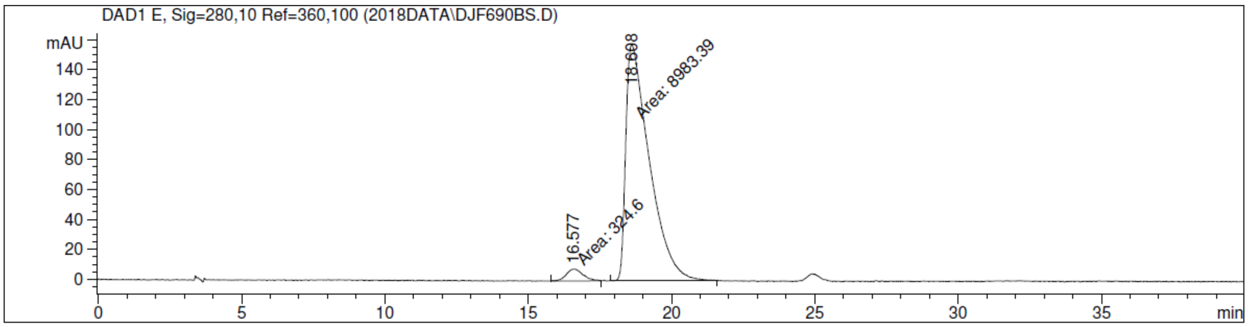
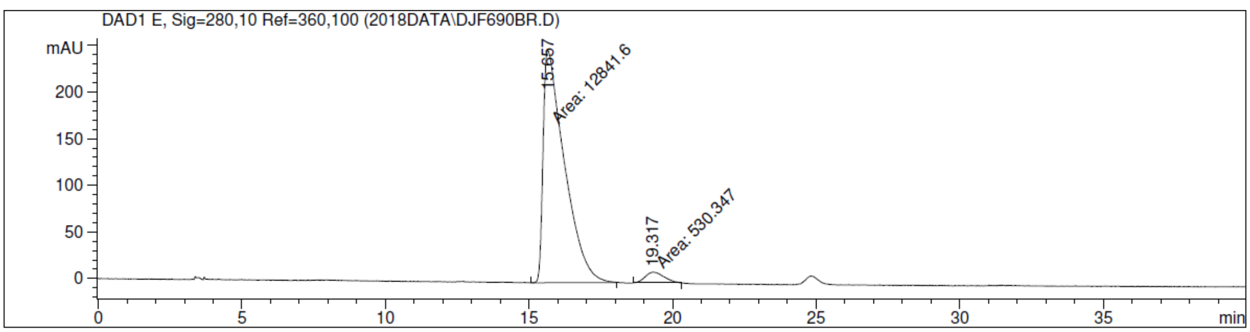


Figure 4B, entry 47

(*S*,*S*)–**L2**: 93% ee
(*R*,*R*)–**L2**: 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.577	MM	0.6790	324.60034	7.96730	3.4873
2	18.608	MM	0.9524	8983.38965	157.20442	96.5127



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.657	MM	0.8584	1.28416e4	249.32965	96.0339
2	19.317	MM	0.7606	530.34662	11.62109	3.9661

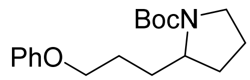
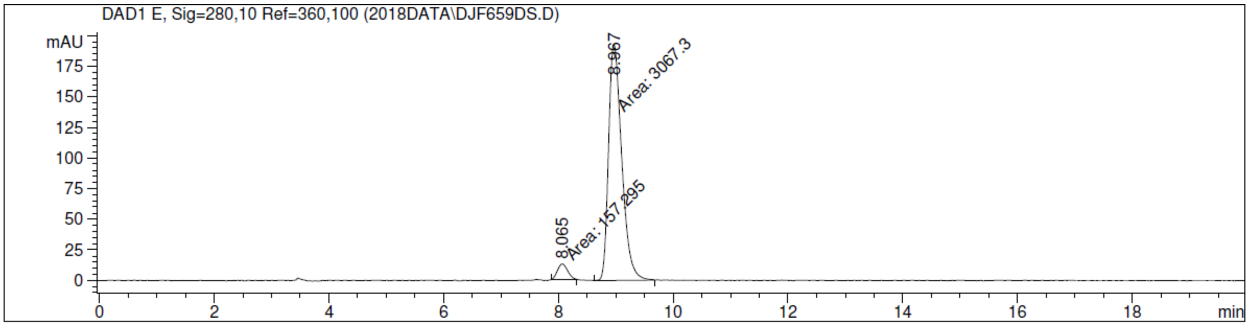
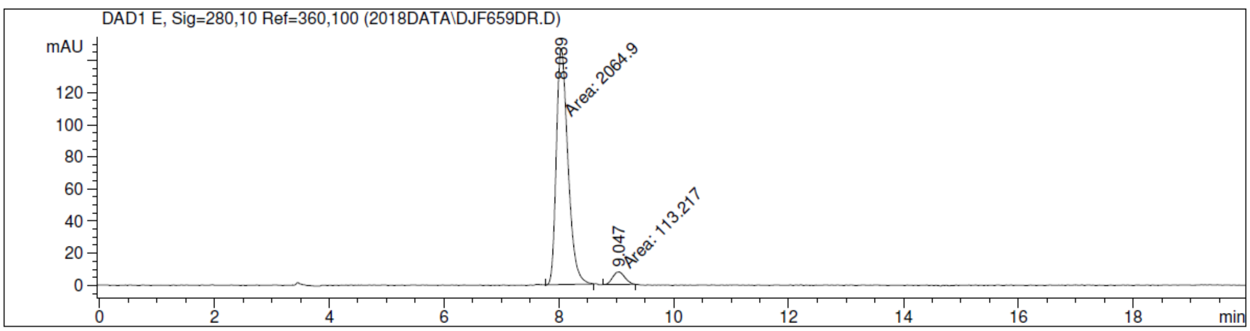


Figure 4B, entry 48

(*S*,*S*)–**L2**: 90% ee
(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.065	MM	0.2067	157.29471	12.68012	4.8780
2	8.967	MM	0.2650	3067.29932	192.88911	95.1220



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.039	MM	0.2347	2064.89990	146.66364	94.8021
2	9.047	MM	0.2431	113.21703	7.76168	5.1979

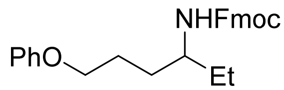
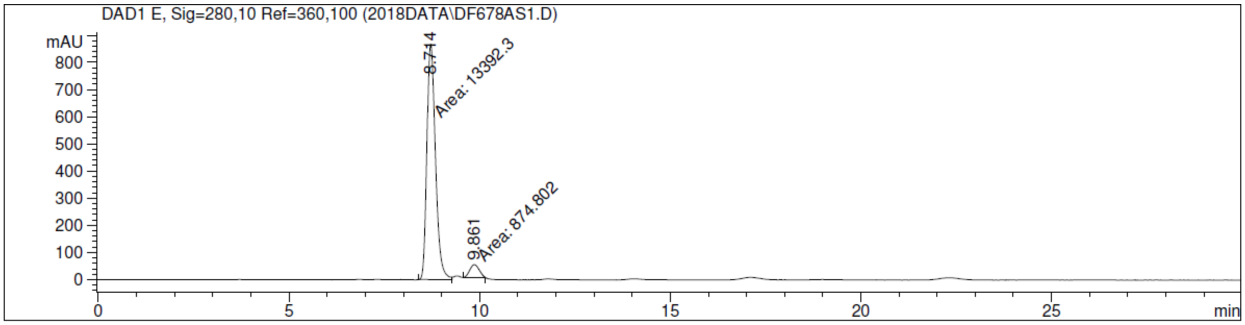
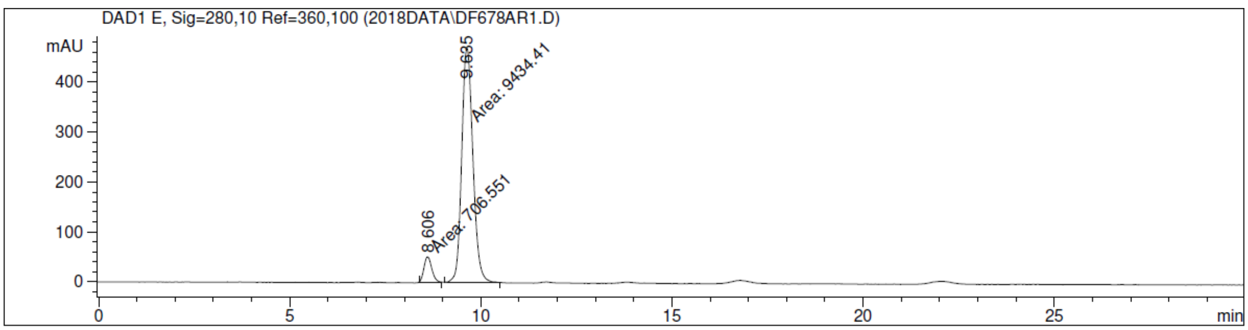


Figure 4B, entry 49

(*S*,*S*)–**L2**: 88% ee
(*R*,*R*)–**L2**: 86% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.714	MM	0.2575	1.33923e4	866.84131	93.8684
2	9.861	MM	0.2968	874.80243	49.11676	6.1316



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.606	MM	0.2321	706.55066	50.73242	6.9673
2	9.635	MM	0.3354	9434.40527	468.77383	93.0327

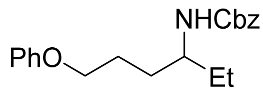
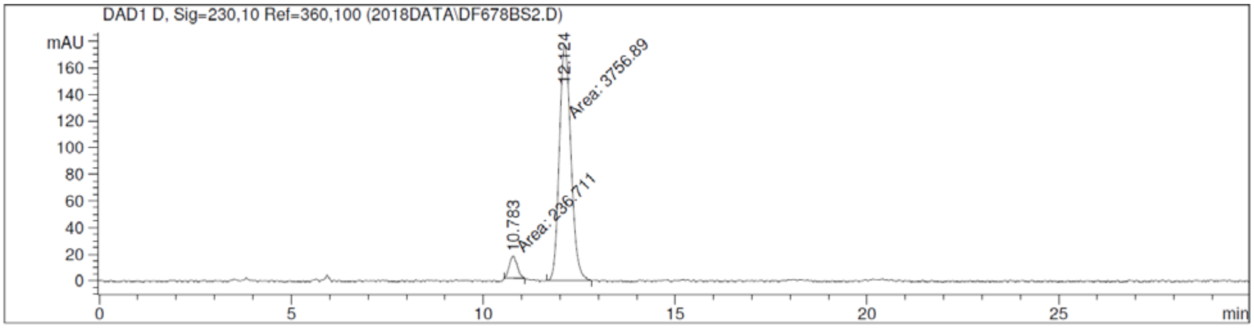


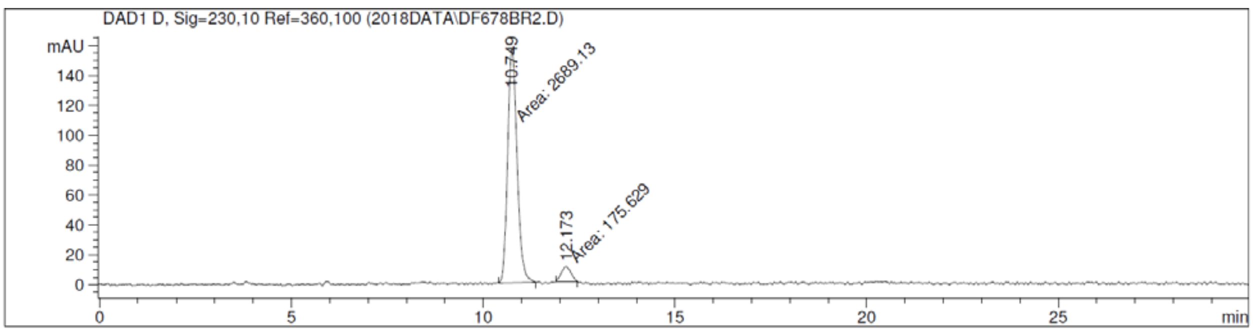
Figure 4B, entry 50

(*S*,*S*)–**L2**: 88% ee

(*R*,*R*)–**L2**: 88% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.783	MM	0.2376	236.71133	16.60091	5.9273
2	12.124	MM	0.3533	3756.88672	177.20412	94.0727



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.749	MM	0.2856	2689.13184	156.91653	93.8693
2	12.173	MM	0.2877	175.62904	10.17385	6.1307

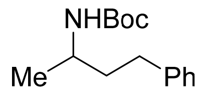
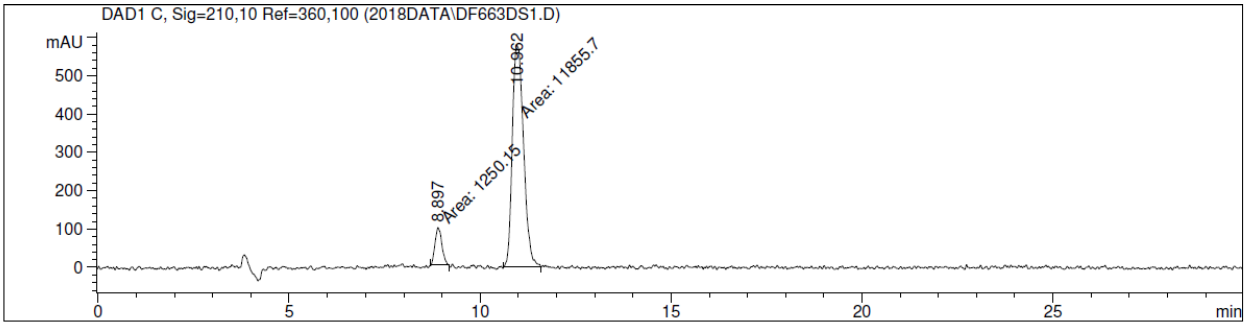
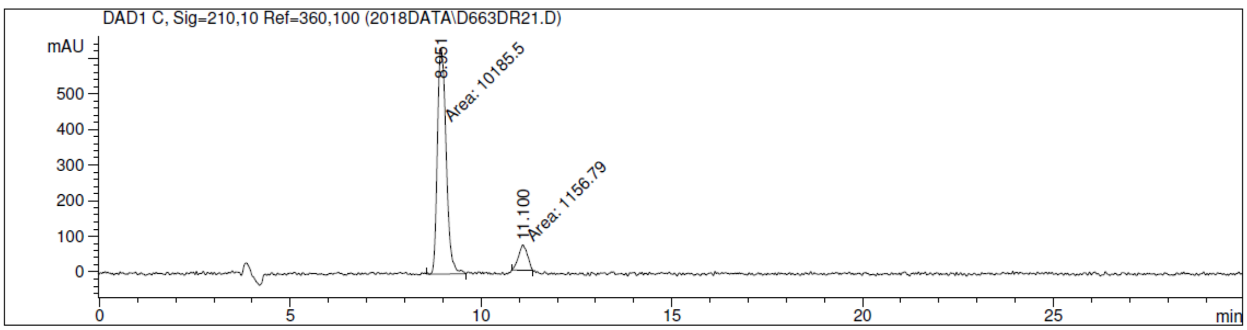


Figure 4B, entry 51

(*S*,*S*)–**L2**: 81% ee
(*R*,*R*)–**L2**: 80% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.897	MM	0.2112	1250.15295	98.64172	9.5389
2	10.962	MM	0.3415	1.18557e4	578.65094	90.4611



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.951	MM	0.2682	1.01855e4	632.87274	89.8011
2	11.100	MM	0.2707	1156.78882	71.22497	10.1989

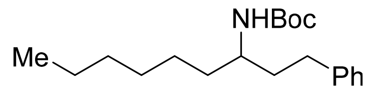
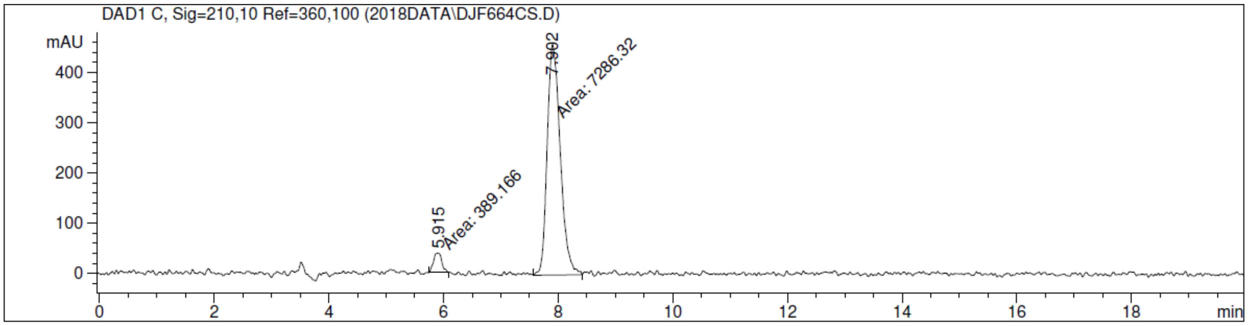


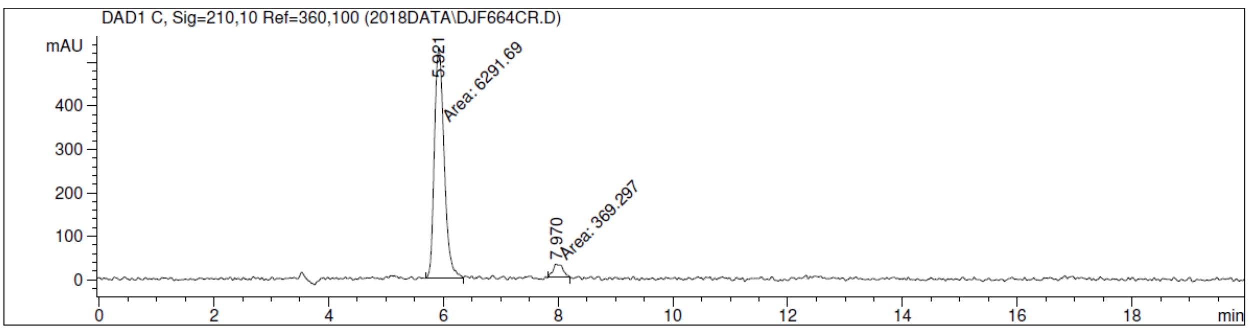
Figure 4B, entry 52

(*S*,*S*)–**L2**: 90% ee

(*R*,*R*)–**L2**: 89% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.915	MM	0.1695	389.16595	38.25952	5.0702
2	7.902	MM	0.2645	7286.32373	459.15646	94.9298



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.921	MM	0.1982	6291.69238	528.94092	94.4558
2	7.970	MM	0.1998	369.29663	30.79893	5.5442

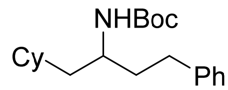
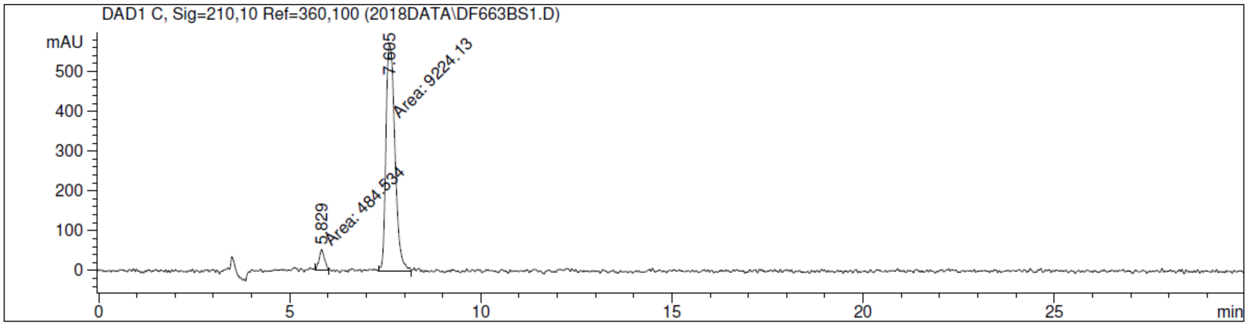
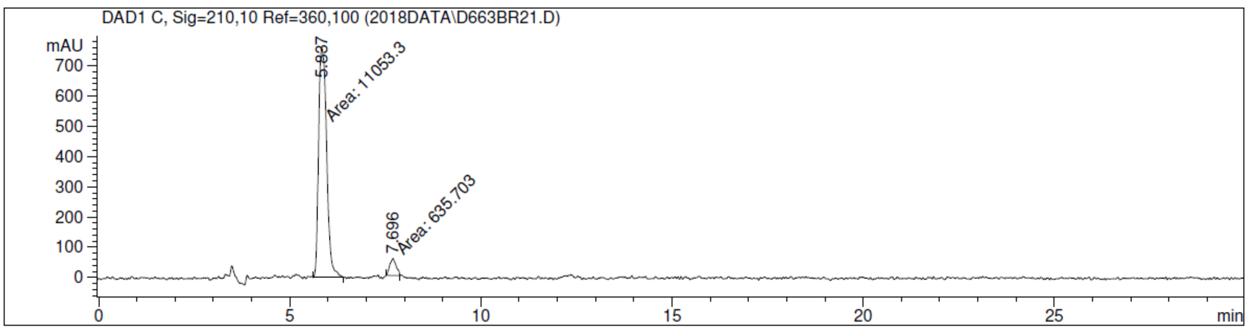


Figure 4B, entry 53

(*S*,*S*)–**L2**: 90% ee
(*R*,*R*)–**L2**: 89% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.829	MM	0.1591	484.53421	50.75657	4.9907
2	7.605	MM	0.2697	9224.12891	570.12939	95.0093



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.837	MM	0.2427	1.10533e4	758.93433	94.5615
2	7.696	MM	0.1878	635.70319	56.41446	5.4385

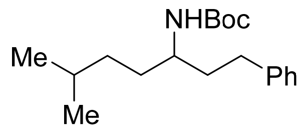
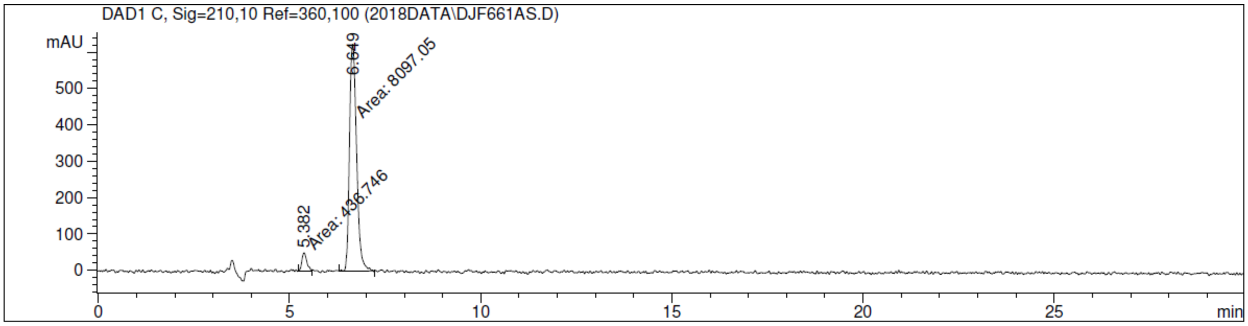
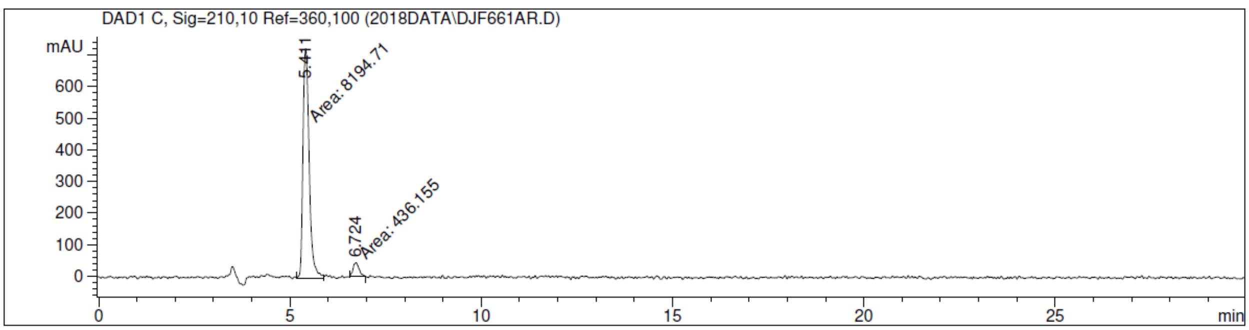


Figure 4B, entry 54

(*S*,*S*)–**L2**: 90% ee
(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.382	MM	0.1486	436.74585	48.97013	5.1178
2	6.649	MM	0.2164	8097.04980	623.72278	94.8822



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.411	MM	0.1885	8194.71387	724.69305	94.9466
2	6.724	MM	0.1707	436.15491	42.59472	5.0534

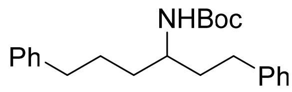
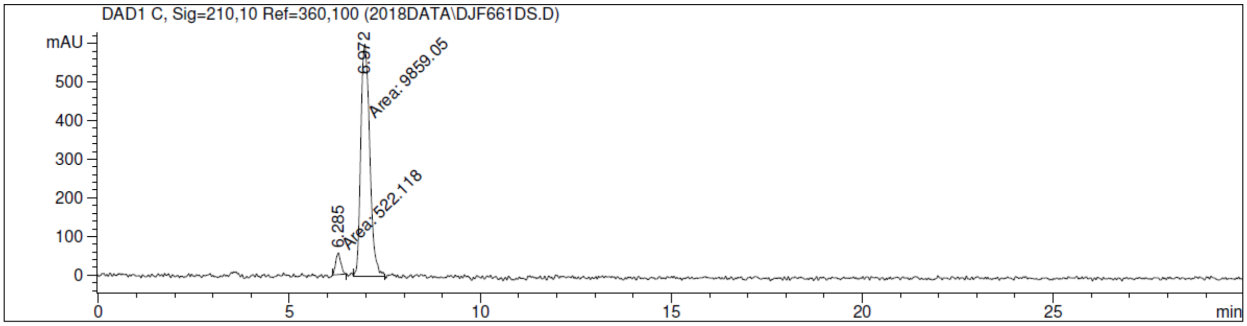
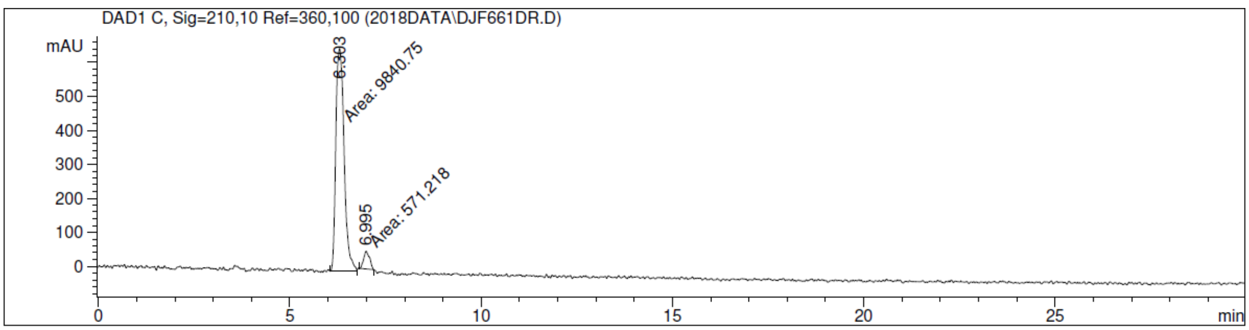


Figure 4B, entry 55

(*S*,*S*)–**L2**: 90% ee
(*R*,*R*)–**L2**: 89% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.285	MM	0.1546	522.11780	56.28405	5.0295
2	6.972	MM	0.2735	9859.04590	600.76782	94.9705



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.303	MM	0.2502	9840.74512	655.59149	94.5138
2	6.995	MM	0.1796	571.21844	53.00961	5.4862

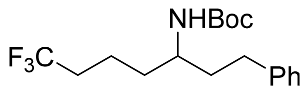
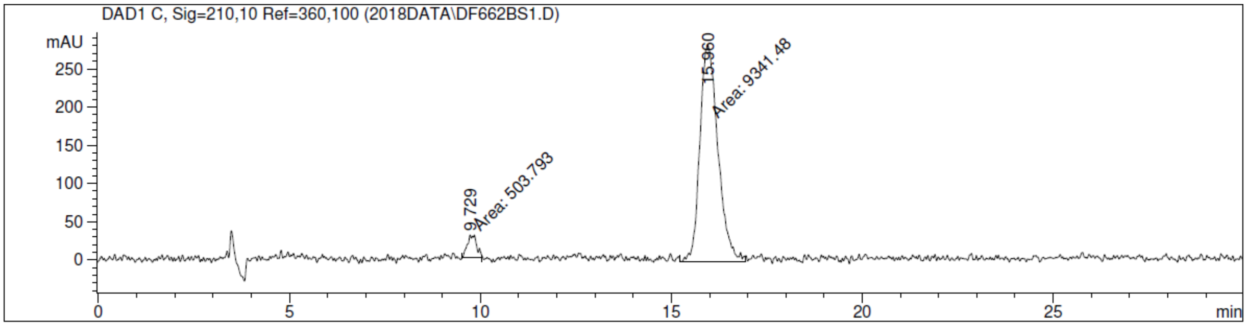
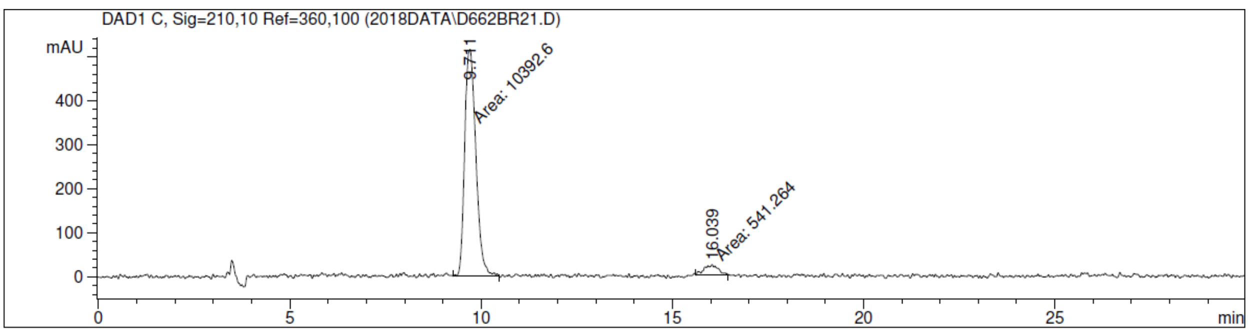


Figure 4B, entry 56

(*S*,*S*)–**L2**: 90% ee
(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.729	MM	0.2816	503.79306	29.82073	5.1171
2	15.960	MM	0.5480	9341.48145	284.12283	94.8829



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.711	MM	0.3361	1.03926e4	515.33710	95.0497
2	16.039	MM	0.4032	541.26447	22.37234	4.9503

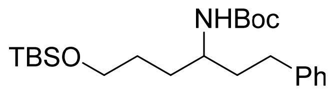
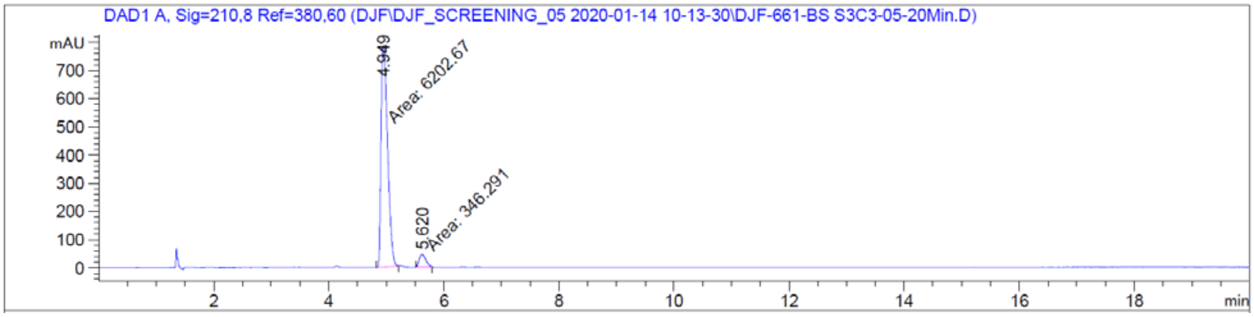


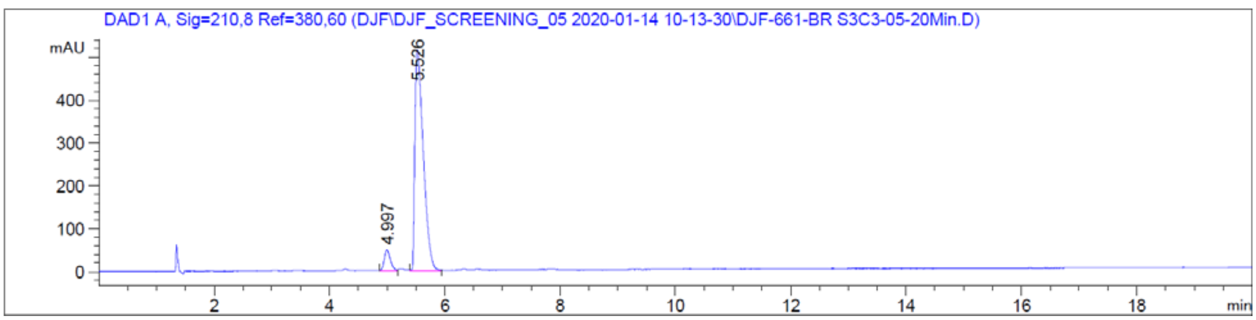
Figure 4B, entry 57

(*S*,*S*)–**L2**: 89% ee

(*R*,*R*)–**L2**: 87% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.949	MM	0.1315	6202.67432	785.97968	94.7123
2	5.620	MM	0.1312	346.29056	43.98158	5.2877



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.997	BV	0.1134	346.88647	47.94778	6.2628
2	5.526	BB	0.1539	5191.99072	513.89722	93.7372

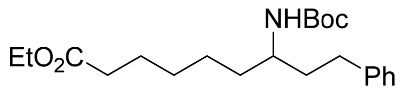
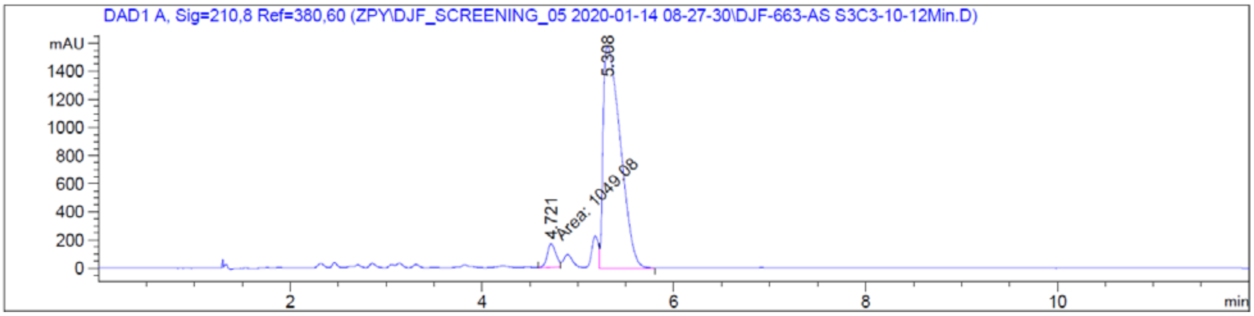


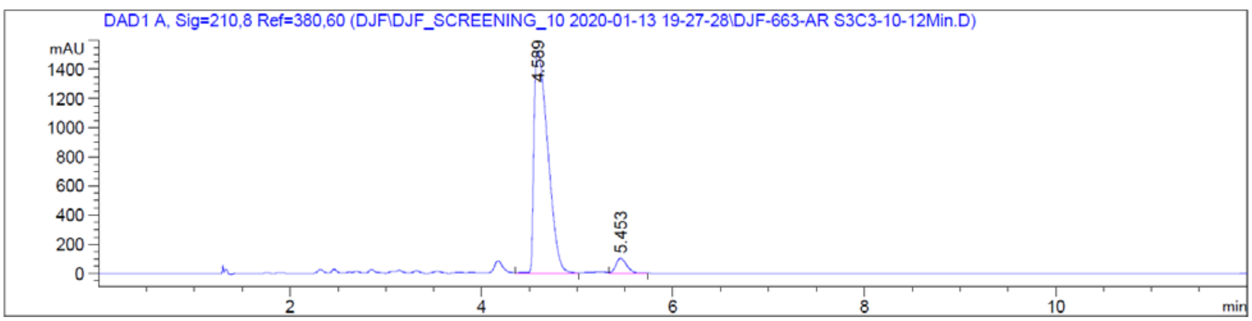
Figure 4B, entry 58

(*S*,*S*)–**L2**: 90% ee

(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.721	MM	0.1043	1049.08203	167.68756	5.0821
2	5.308	VB	0.1967	1.95935e4	1579.65479	94.9179



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.589	VV	0.1612	1.53247e4	1525.14880	95.0005
2	5.453	VB	0.1219	806.47241	102.34901	4.9995

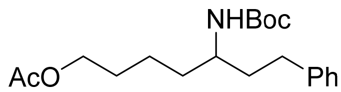
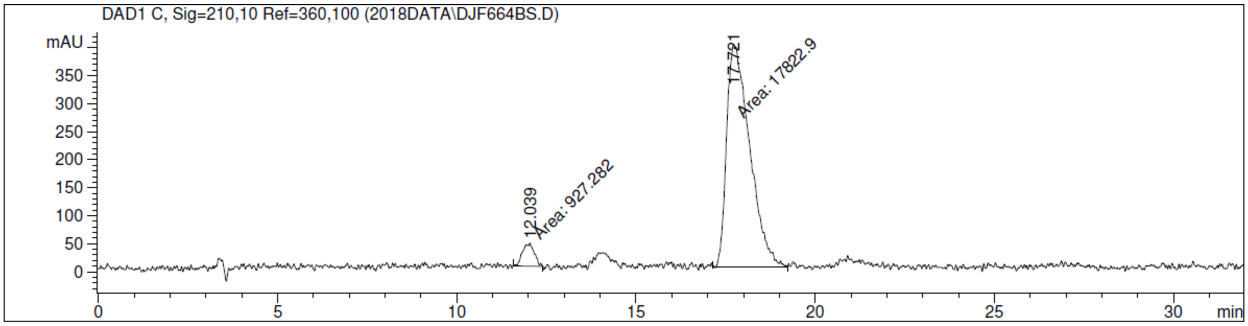
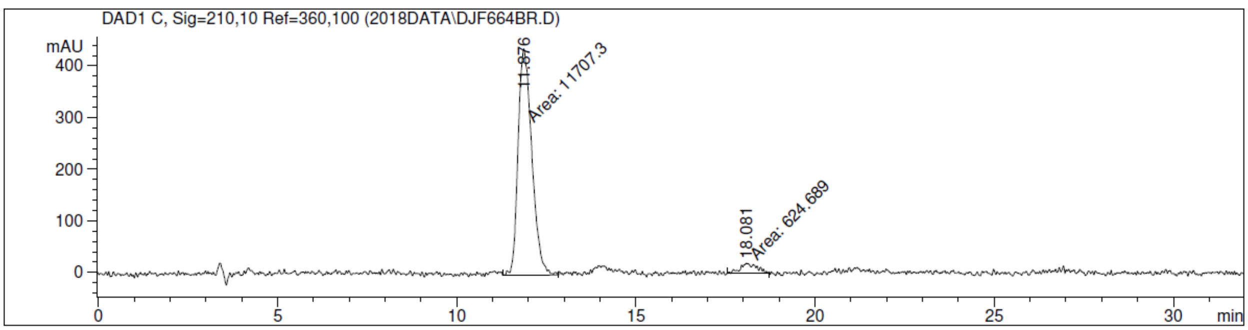


Figure 4B, entry 59

(*S*,*S*)–**L2**: 90% ee
(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.039	MM	0.3741	927.28217	41.31146	4.9455
2	17.721	MM	0.7454	1.78229e4	398.53409	95.0545



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.876	MM	0.4456	1.17073e4	437.87848	94.9344
2	18.081	MM	0.5304	624.68890	19.62891	5.0656

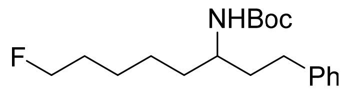
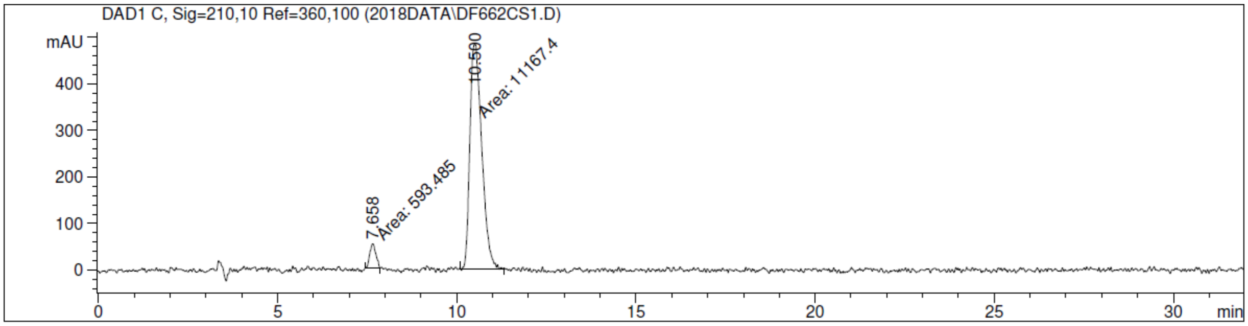
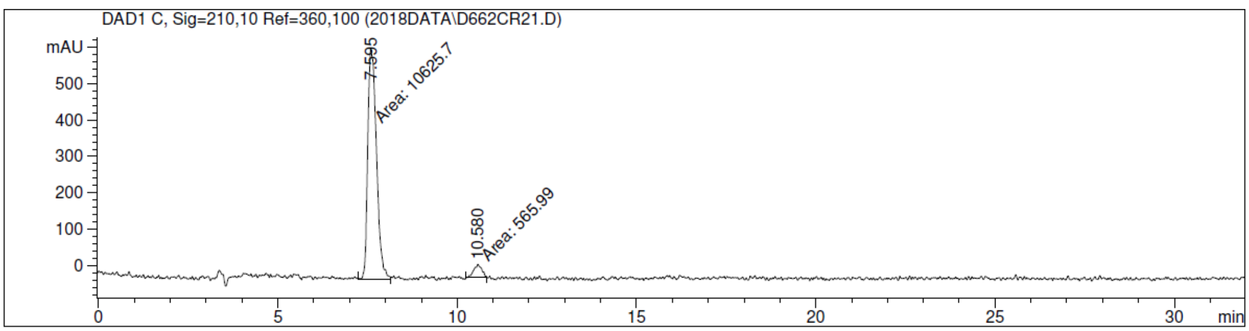


Figure 4B, entry 60

(*S*,*S*)–**L2**: 90% ee
(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.658	MM	0.1924	593.48462	51.40942	5.0463
2	10.500	MM	0.3849	1.11674e4	483.58502	94.9537



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.595	MM	0.2808	1.06257e4	630.58209	94.9428
2	10.580	MM	0.2582	565.98950	36.53745	5.0572

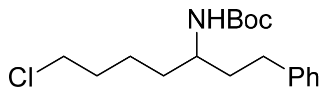
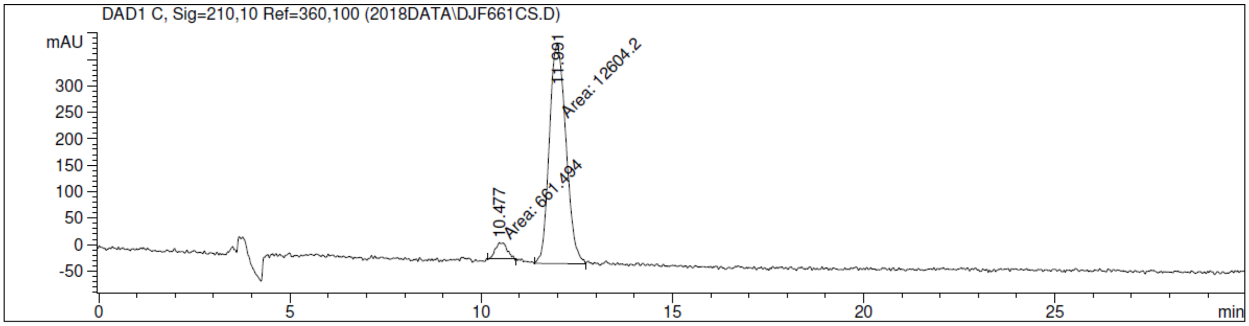


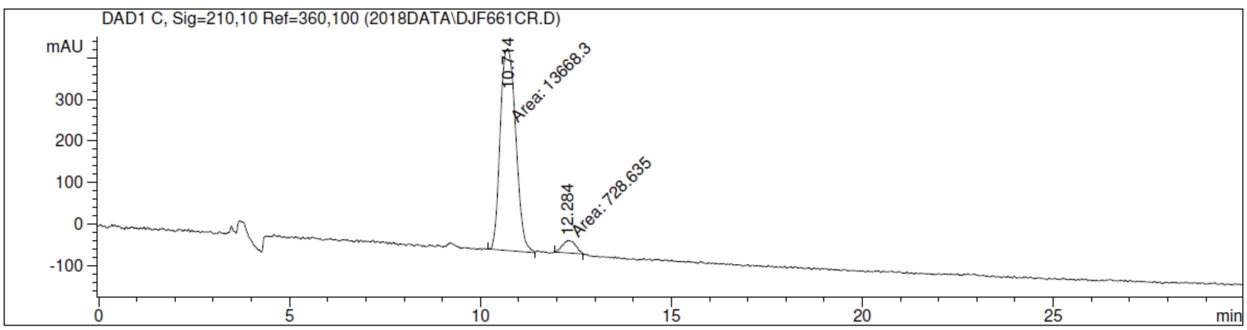
Figure 4B, entry 61

(*S*,*S*)–**L2**: 90% ee

(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.477	MM	0.3532	661.49377	31.21469	4.9865
2	11.991	MM	0.5067	1.26042e4	414.60278	95.0135



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.714	MM	0.4685	1.36683e4	486.28604	94.9390
2	12.284	MM	0.3998	728.63501	30.37362	5.0610

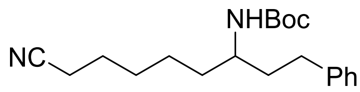
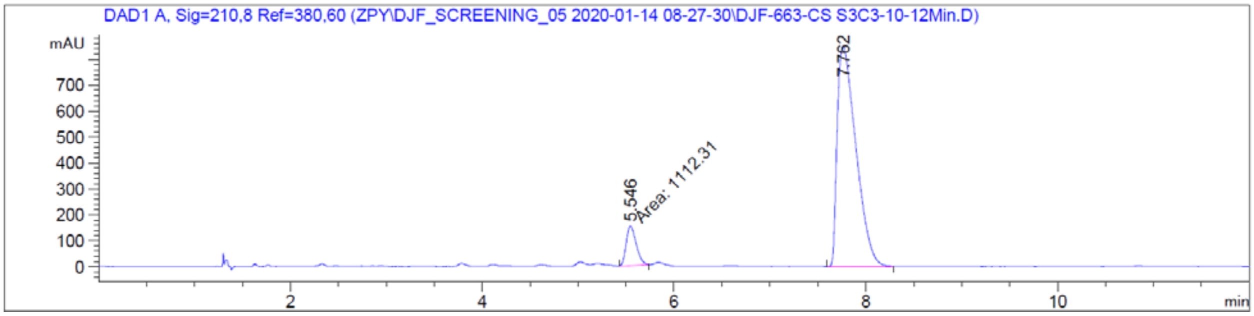


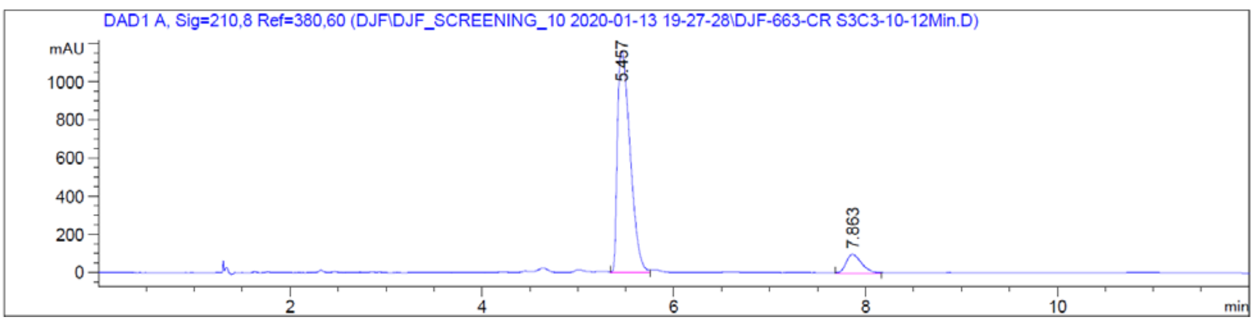
Figure 4B, entry 62

(*S*,*S*)–**L2**: 82% ee

(*R*,*R*)–**L2**: 82% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.546	MM	0.1219	1112.30969	152.10696	8.8017
2	7.762	BB	0.2098	1.15252e4	852.09442	91.1983



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.457	VV	0.1474	1.06958e4	1161.51941	91.1079
2	7.863	BB	0.1617	1043.91333	96.87712	8.8921

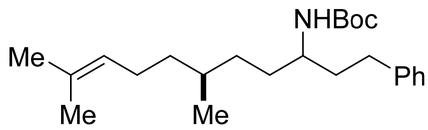
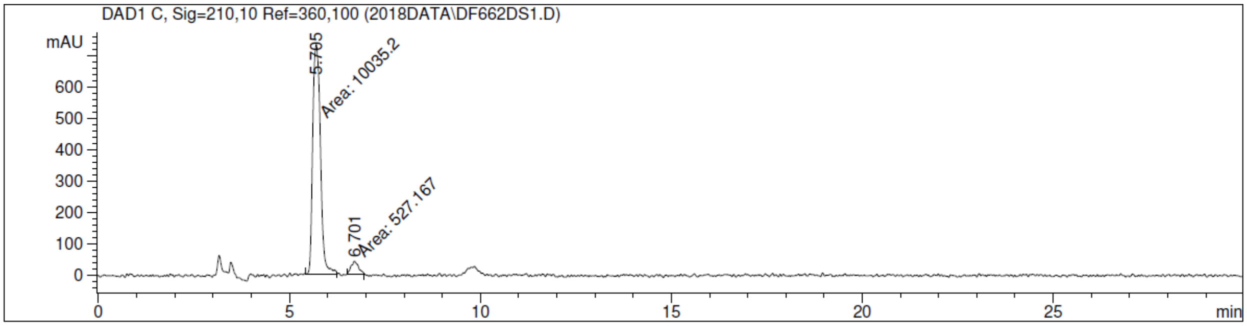
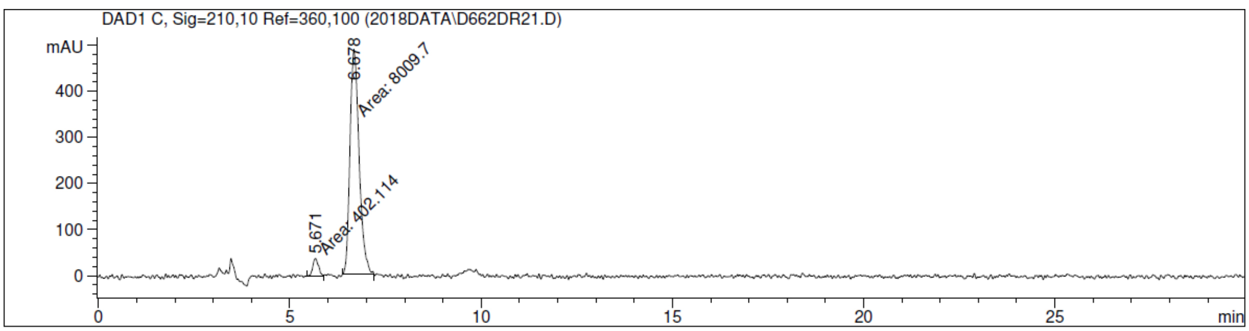


Figure 4B, entries 64 and 63

(*S*,*S*)–**L2**: 5:95 dr
(*R*,*R*)–**L2**: 95:5 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.705	MM	0.2285	1.00352e4	731.90674	95.0090
2	6.701	MM	0.2130	527.16650	41.24250	4.9910



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.671	MM	0.1721	402.11411	38.94483	4.7803
2	6.678	MM	0.2733	8009.70068	488.49478	95.2197

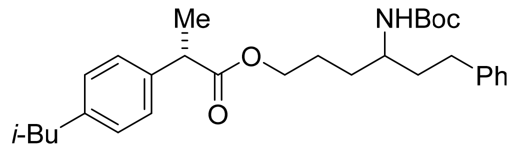
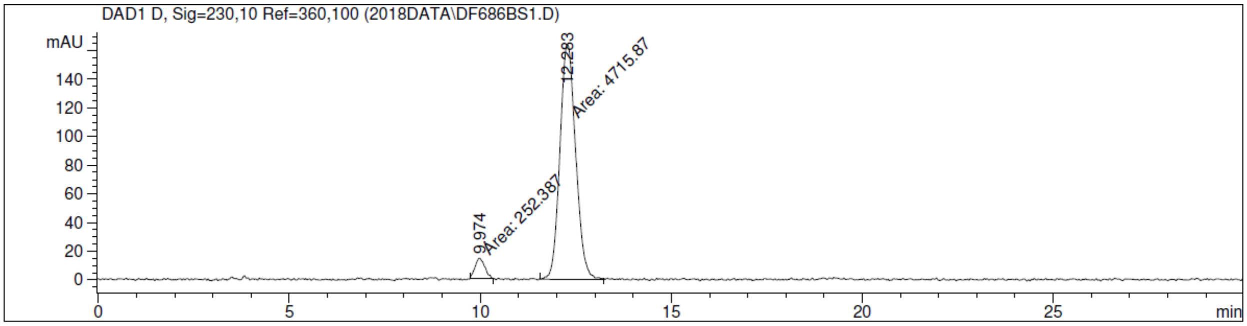
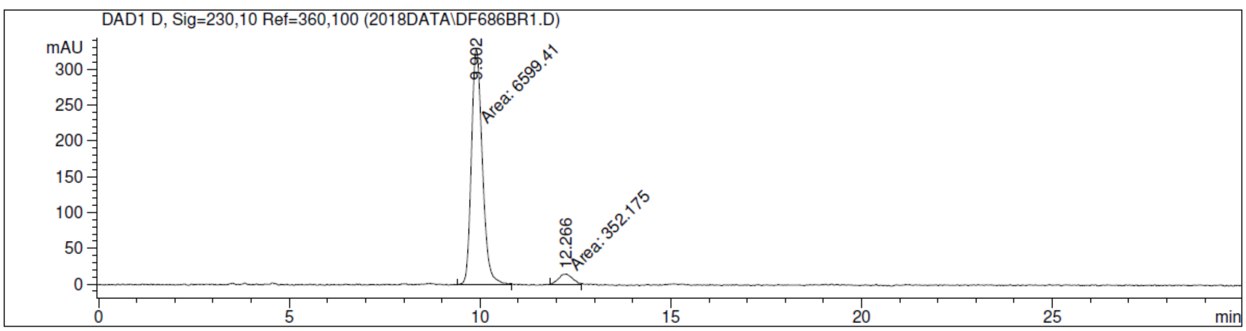


Figure 4B, entries 66 and 65

(*S*,*S*)–**L2**: 5:95 dr
(*R*,*R*)–**L2**: 95:5 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.974	MM	0.2976	252.38727	14.13593	5.0800
2	12.283	MM	0.4788	4715.87305	164.14810	94.9200



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.902	MM	0.3356	6599.40771	327.75955	94.9339
2	12.266	MM	0.4142	352.17523	14.16951	5.0661

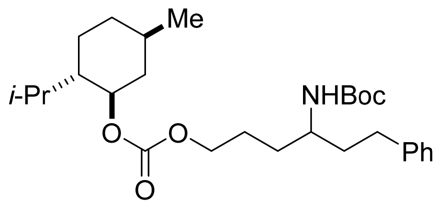
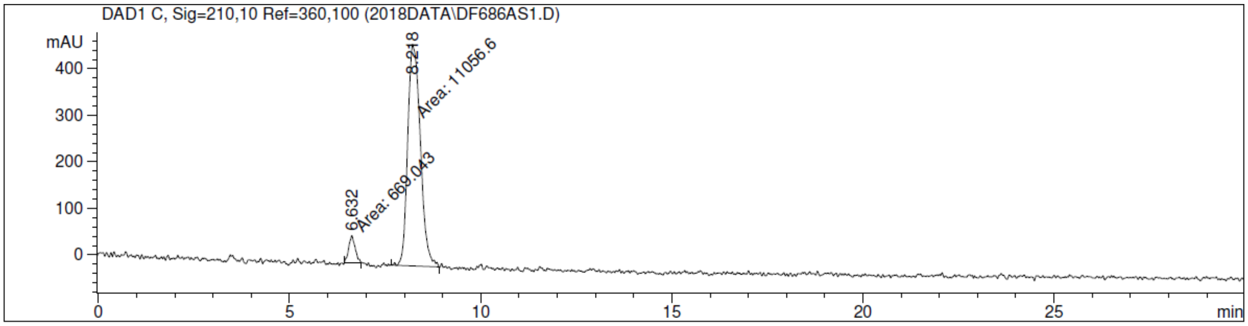
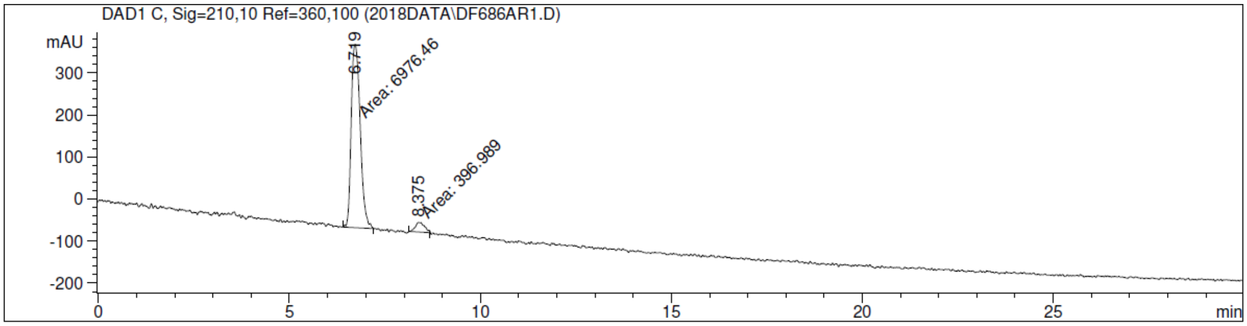


Figure 4B, entries 68 and 67

(*S*,*S*)–**L2**: 6:94 dr
(*R*,*R*)–**L2**: 95:5 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.632	MM	0.1899	669.04303	58.70404	5.7058
2	8.218	MM	0.3863	1.10566e4	477.03387	94.2942



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.719	MM	0.2666	6976.46240	436.05872	94.6160
2	8.375	MM	0.2864	396.98920	23.10586	5.3840

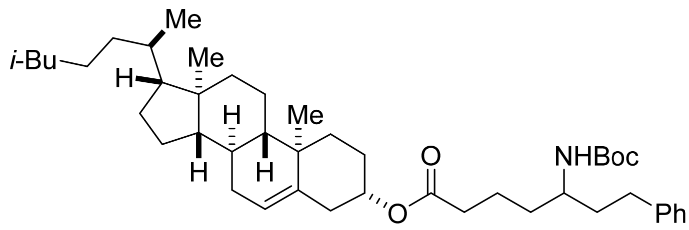
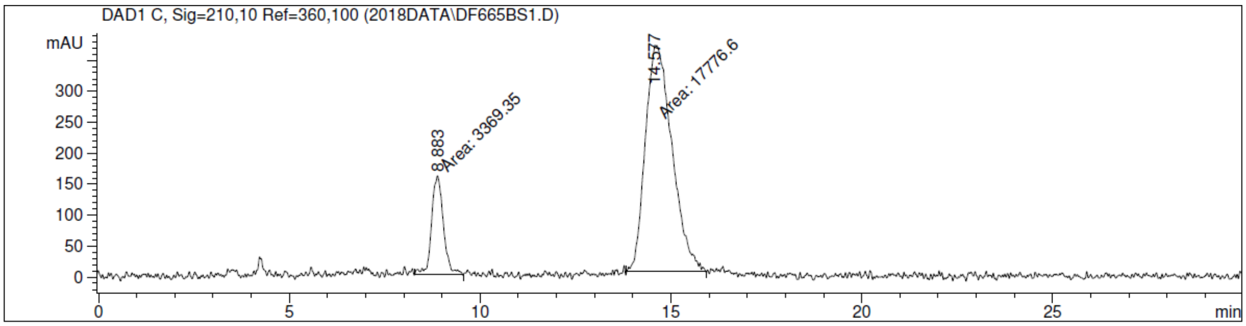
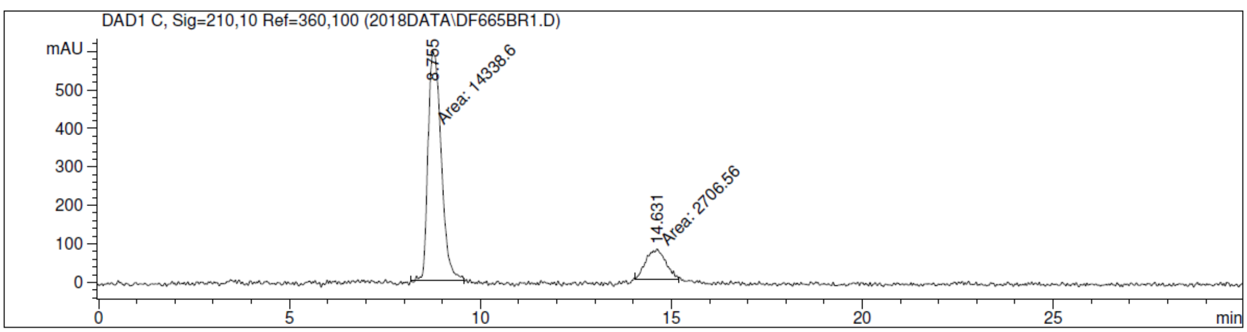


Figure 4B, entries 70 and 69

(*S*,*S*)–**L2**: 16:84 dr
(*R*,*R*)–**L2**: 84:16 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.883	MM	0.3549	3369.34766	158.24919	15.9338
2	14.577	MM	0.8106	1.77766e4	365.51141	84.0662



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.755	MM	0.3995	1.43386e4	598.13202	84.1212
2	14.631	MM	0.5831	2706.55640	77.36240	15.8788

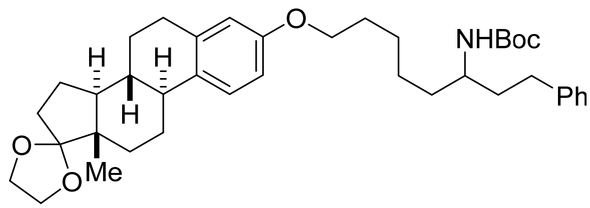
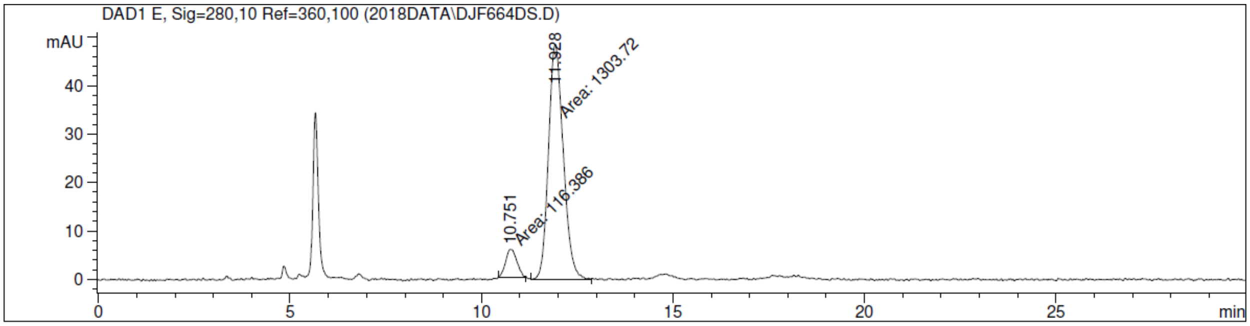
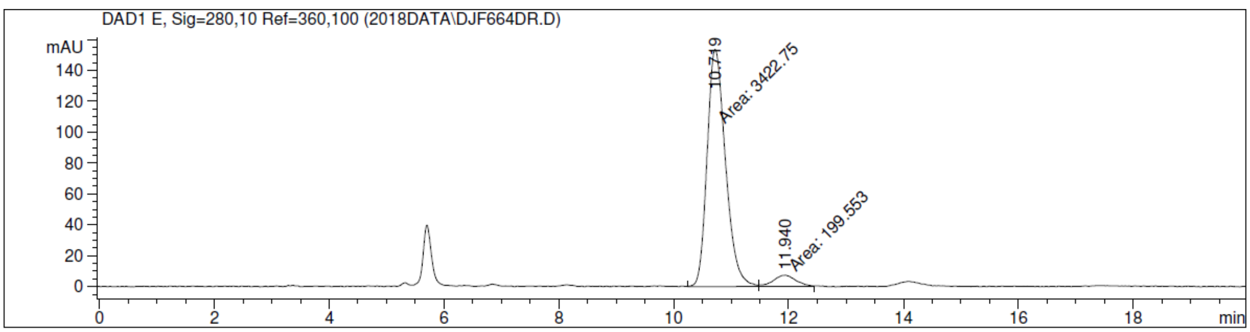


Figure 4B, entries 72 and 71

(*S*,*S*)–**L2**: 8:92 dr
(*R*,*R*)–**L2**: 94:6 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.751	MM	0.3395	116.38594	5.71287	8.1956
2	11.928	MM	0.4477	1303.72192	48.53754	91.8044



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.719	MF	0.3712	3422.74829	153.67122	94.4910
2	11.940	FM	0.4524	199.55276	7.35124	5.5090

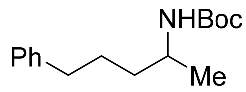
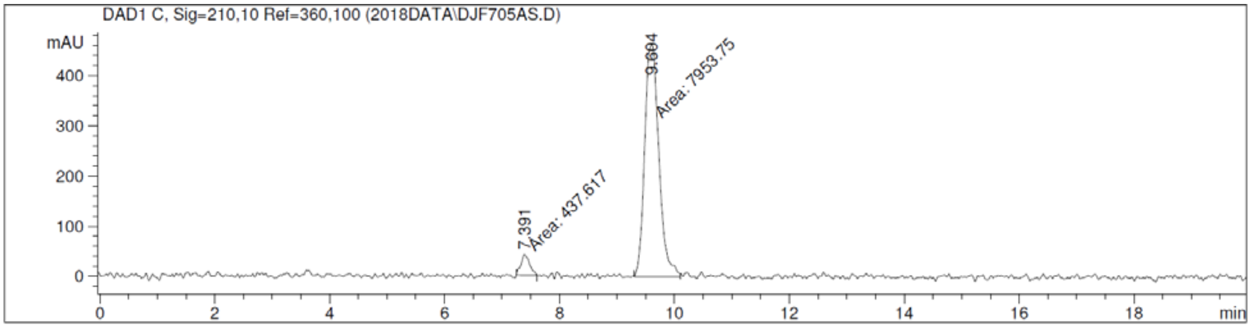
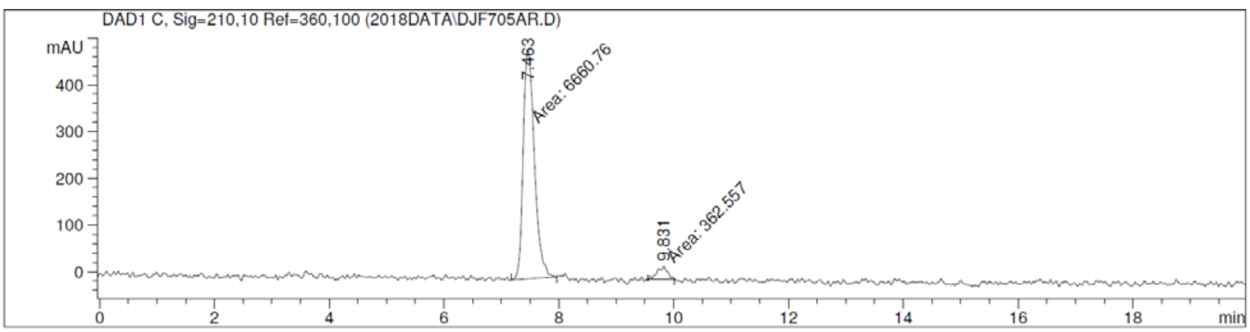


Figure 5B, entry 73

(*S*,*S*)–**L2**: 90% ee
(*R*,*R*)–**L2**: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.391	MM	0.1756	437.61670	41.54410	5.2151
2	9.604	MM	0.2869	7953.75342	462.06326	94.7849



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.463	MM	0.2262	6660.75781	490.68774	94.8378
2	9.831	MM	0.2097	362.55688	28.81344	5.1622

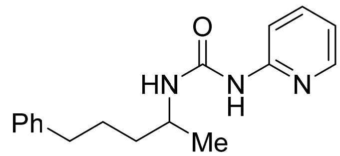
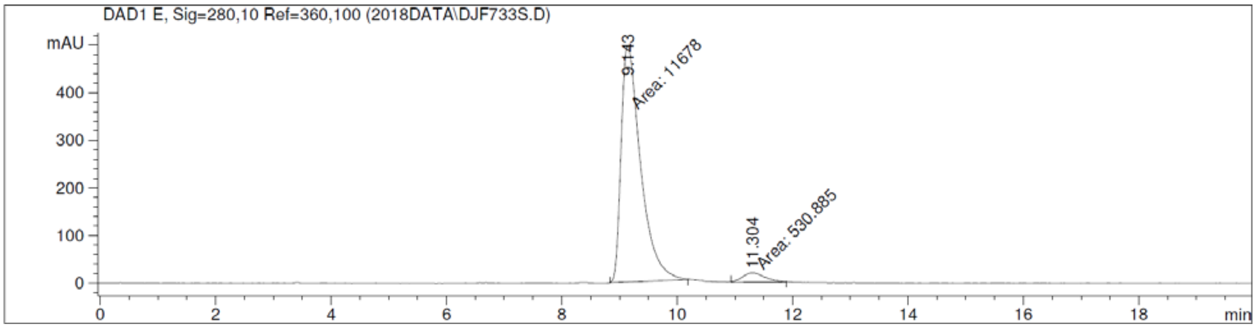
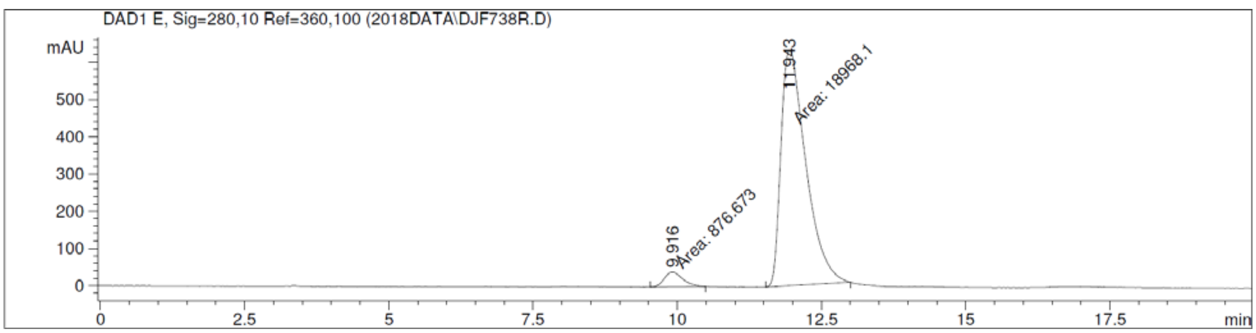


Figure 5B, entry 74

(*S*,*S*)–**L2**: 91% ee
(*R*,*R*)–**L2**: 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.143	MM	0.3913	1.16780e4	497.43579	95.6517
2	11.304	MM	0.4473	530.88458	19.78203	4.3483



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.916	MM	0.3718	876.67328	39.29351	4.4176
2	11.943	MM	0.4996	1.89681e4	632.81482	95.5824

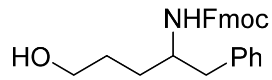
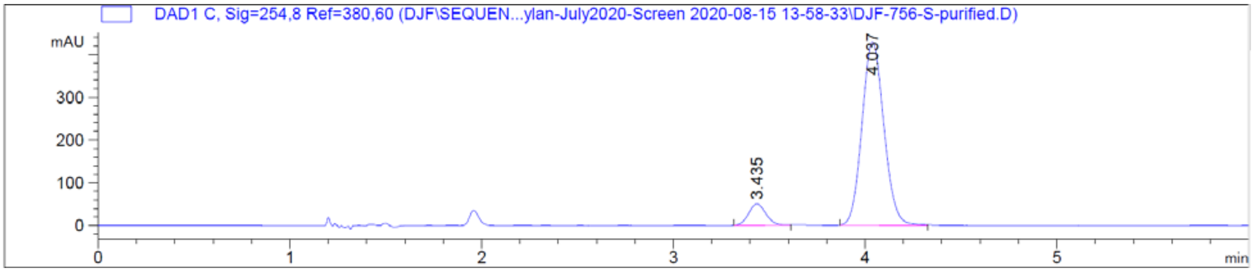
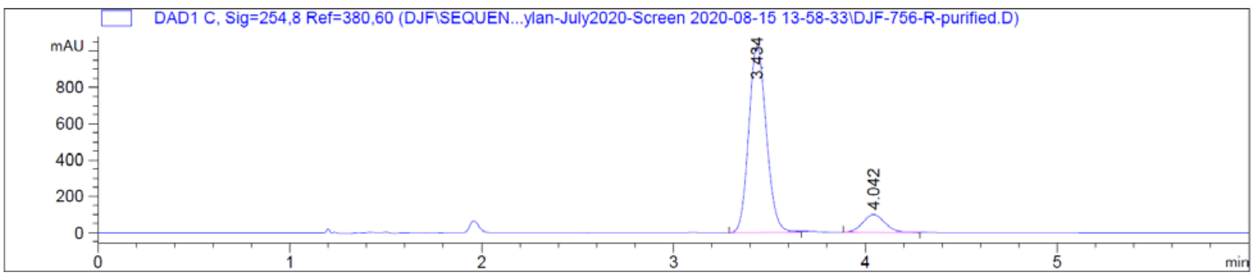


Figure 5B, entry 75

(*S*,*S*)–**L2**: 83% ee
(*R*,*R*)–**L2**: 79% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.435	BB	0.0983	314.07040	49.96241	8.4538
2	4.037	BB	0.1246	3401.04688	428.63629	91.5462



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.434	BB	0.0993	6526.82422	1025.27502	89.2856
2	4.042	BB	0.1245	783.23035	97.68038	10.7144

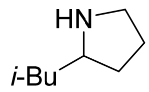
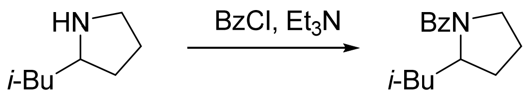
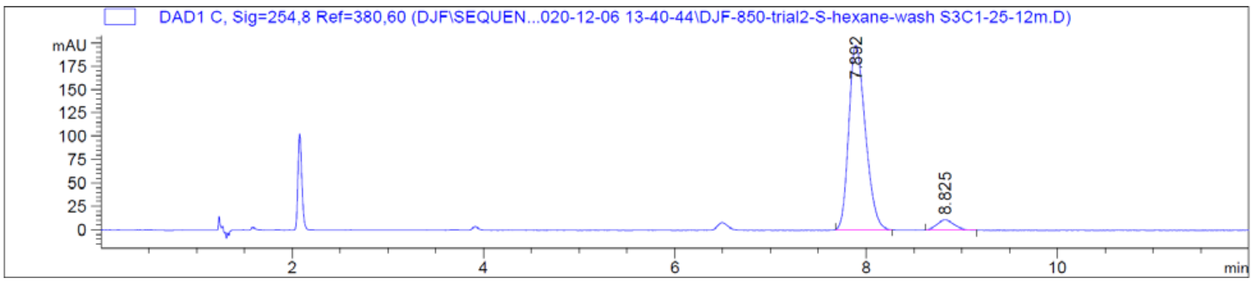


Figure 5B, entry 76

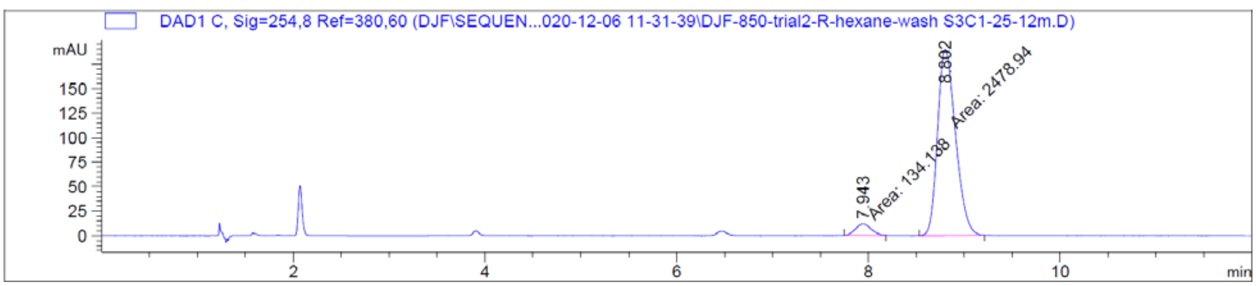
(*S*,*S*)–**L2**: 89% ee
(*R*,*R*)–**L2**: 90% ee

Determination of the ee:





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.892	BB	0.1882	2390.17871	197.46819	94.6575
2	8.825	BB	0.1965	134.90157	10.66684	5.3425



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.943	MM	0.1905	134.13777	11.73663	5.1333
2	8.802	MM	0.2176	2478.93945	189.82697	94.8667

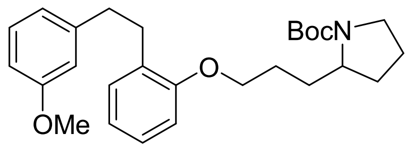
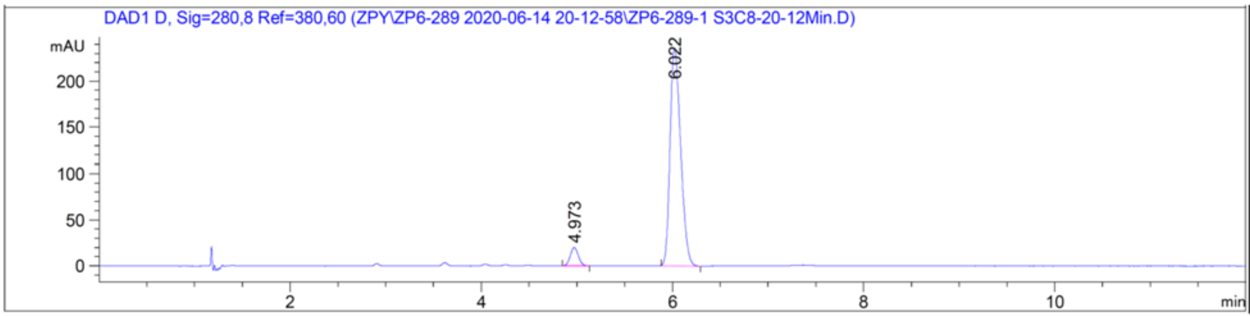
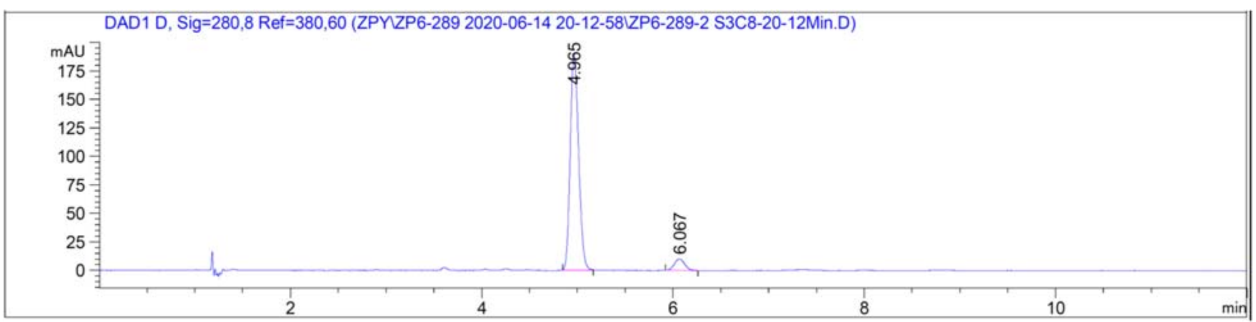


Figure 5B, entry 77

(*S*,*S*)–**L2**: 88% ee
(*R*,*R*)–**L2**: 88% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.973	BB	0.0933	118.71468	19.99634	6.1185
2	6.022	BB	0.1210	1821.55359	236.22536	93.8815



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.965	BB	0.0943	1164.51855	190.58186	93.9544
2	6.067	BB	0.1158	74.93285	10.06825	6.0456